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# JOURNAL OF INORGANIC AND NUCLEAR CHEMISTRY



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# THE PURIFICATION AND ABSOLUTE DETERMINATION OF $^{99}$Mo AND THE NEUTRON CAPTURE CROSS-SECTION OF $^{98}$Mo

M. J. CABELL
Atomic Energy Research Establishment, Harwell, Didcot, Berks.

(*Received* 20 *February* 1961)

**Abstract**—Procedures are described for (a) the purification of neutron-irradiated, enriched $^{98}$Mo by anion exchange chromatography and (b) the absolute determination of $^{99}$Mo. These procedures are used in a determination of the reactor and thermal neutron capture cross-sections and the resonance capture integral of $^{98}$Mo by an activation method.

Assuming 98·8 barns for the thermal neutron capture cross-section of $^{197}$Au, values of $\hat{\sigma} = 0{\cdot}377 \pm 0{\cdot}007$ barns (for $r\sqrt{(T/T_0)} = 0{\cdot}032$) and $\sigma_0 = 0{\cdot}136 \pm 0{\cdot}003$ barns have been obtained for $^{98}$Mo. The resonance capture integral (from 0·5 eV to $\infty$) was found to be $6{\cdot}69 \pm 0{\cdot}13$ barns relative to 1558 barns for the resonance capture integral of $^{197}$Au.

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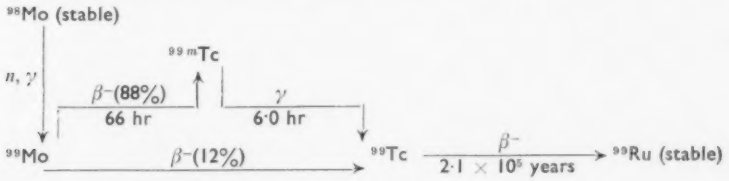
ALTHOUGH the yield of $^{98}$Mo in fission is high (5·78 per cent in the thermal neutron fission of $^{235}$U),[1] its neutron capture cross-section is not known precisely and, in consequence, the effect of its presence on the reactivity of nuclear fuel rods cannot be calculated with any certainty.

In 1947, SEREN *et al.*,[2] using an activation method, found a neutron capture cross-section of $0{\cdot}415 \pm 0{\cdot}083$ barns in a reactor spectrum of unspecified epi-thermal content. POMERANCE[3] in 1952, using a pile oscillator and an essentially thermal neutron spectrum, obtained the figure $0{\cdot}4 \pm 0{\cdot}4$ barns. Also in 1952, the first comprehensive American compilation of cross-section data[4] quoted $0{\cdot}13 \pm 0{\cdot}05$ barns for the thermal neutron capture cross-section, this figure being obtained by an activation method, details of which were not published. In 1958,[5] this last figure was amended to $0{\cdot}45 \pm 0{\cdot}10$ barns, and in 1960[6] to $0{\cdot}51 \pm 0{\cdot}06$ barns, although in neither case were further details given. No measurements of differential cross-sections or of the resonance capture integral of this isotope have so far been reported in the literature.

This present paper describes an activation method used for the determination of the capture cross-section of $^{98}$Mo for reactor and thermal neutrons and for the determination of its resonance capture integral.

The following nuclear reactions are involved:




[1] S. KATCOFF, *Nucleonics* **16**, 75 (1958).
[2] L. SEREN, H. N. FRIEDLANDER and S. H. TURKEL, *Phys. Rev.* **72**, 88 (1947).
[3] H. POMERANCE, *Phys. Rev.* **88**, 413 (1952).
[4] M. D. GOLDBERG and J. A. HARVEY, U.S.A.E.C. Unclassified Report A.E.C.U. 2040 (1952).
[5] D. J. HUGHES and R. B. SCHWARTZ, Brookhaven National Laboratory Report, BNL 325 (2nd Ed.) (1958).
[6] D. J. HUGHES, B. A. MAGURNO and M. K. BRUSSEL, Brookhaven National Laboratory Report, BNL 325 (2nd Ed.) Supplement No. 1(1960).

The method consisted of the irradiation in a lattice position of BEPO of 50 $\mu$l aliquots of a solution containing microgram quantities of enriched $^{98}$Mo (a) unshielded and (b) shielded by 0·068 cm cadmium. Thin gold foils were attached to measure the thermal and epi-cadmium fluxes. After irradiation the molybdenum was separated by anion exchange chromatography both from impurities and from its daughter $^{99}$Tc. Known aliquots were taken from the resulting solution for (a) mounting on thin films for counting and (b) isotopic dilution analysis. The $^{99}$Mo content of each source was then determined from measurements of the change in its absolute $\beta$-disintegration rate with time and the corresponding $^{98}$Mo content of each source was determined from the isotopic dilution analyses.

This method has two valuable features. Firstly, since only microgram quantities are involved, the possibility of self-shielding during the irradiation is eliminated and "weightless" sources for counting are readily prepared. Secondly, since the amount of material in each source is determined *after* purification, the chemical yield during the purification process (which will vary from experiment to experiment) need not be known; in addition the need to determine the purity of the starting material is eliminated also.

## EXPERIMENTAL METHODS

1. *Starting material*

Approximately 10 mg of enriched $^{98}$Mo in the form of molybdenum trioxide were supplied by the Electromagnetic Separation Group of Chemistry Division, A.E.R.E. The sample was dissolved in ten drops of warm concentrated ammonium hydroxide and diluted to 5 ml. Aliquots were taken from this stock for all irradiations. A further aliquot was taken for isotopic analysis (see section on "mass spectrometric measurements") and the molybdenum was found to have the following composition (in atom per cent).

0·99 $\pm$ 0·02 per cent $^{100}$Mo, 93·24 $\pm$ 0·07 per cent $^{98}$Mo,
2·12 $\pm$ 0·05 per cent $^{97}$Mo, 1·49 $\pm$ 0·04 per cent $^{96}$Mo,
0·96 $\pm$ 0·02 per cent $^{95}$Mo, 0·49 $\pm$ 0·02 per cent $^{94}$Mo and
0·71 $\pm$ 0·02 per cent $^{92}$Mo.

2. *Irradiations*

Thin gold monitors were prepared as described by CABELL[7].

Approximately 50 $\mu$l aliquots (containing about 100 $\mu$g $^{98}$Mo) of the stock solution were sealed in silica ampoules, a monitor was wrapped round each ampoule and the two were packed either directly, or enclosed within a 0·068 $\pm$ 0·002 cm thick cadmium box and then packed in a hole drilled in a polythene block which accurately positioned the sample in the nylon rabbit of the pneumatic carrier.

Irradiations were carried out in a lattice position of BEPO for periods between 4·000 and 12·000 hr and were conducted in pairs or triplets during periods of constant pile power. One sample of each group was shielded by cadmium; the others were unshielded.

3. *Purification of irradiated molybdenum*

(a) *Preliminary experiments.* Preliminary experiments involving chemical separations followed by $\gamma$-spectrometry and half-life measurements of the various fractions had identified $^{64}$Cu ($T_{\frac{1}{2}} = 12{\cdot}8$ hr) and $^{187}$W ($T_{\frac{1}{2}} = 24{\cdot}0$ hr), the latter greatly predominating, as the main radioactive impurities in the irradiated molybdenum. In addition to separating the molybdenum from these it was necessary to remove the $^{99m}$Tc daughter which had grown into the irradiated material before counting (see section on "absolute disintegration rate determinations"). This was accomplished by anion-exchange chromatography.

Fig. 1 shows the separation achieved on a 100 mg column of Deacidite FF (for further details see next section). The irradiated sample (50 $\mu$l of dilute ammonia containing 100 $\mu$g $^{98}$Mo) was diluted with 1 ml 8 M hydrochloric acid and fed to the column at a flow rate of four drops per minute. The

[7] M. J. CABELL, *Reactor Sci.* **12**, 172 (1960).

column was then eluted successively with 5 ml 4 M hydrochloric acid, 5 ml M hydrochloric acid and 5 ml 4 M nitric acid, also at a flow-rate of four drops per minute. The effluent was collected throughout in 5-drop aliquots which were dried and counted to give the activity measurements recorded in the figure. The $\gamma$-spectra and half-lives of the activities served to identify the components of the individual peaks and showed them to be in a high state of purity.

The figure shows that the separation of molybdenum from tungsten is almost complete even at the high linear flow-rate employed. The small hump in the elution curve which results from changing the eluent from 1 M hydrochloric acid to 4 M nitric acid is due to "tailing" of the molybdenum into the technetium fraction. Although less than 0·5 per cent of the total molybdenum is involved in this way,

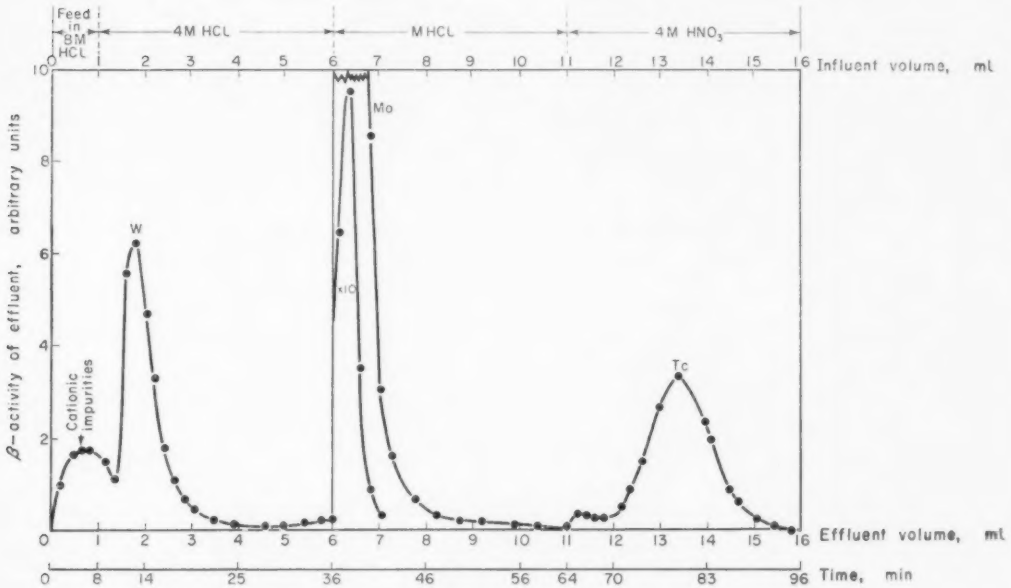



FIG. 1.—Separation of $^{99}$Mo from impurities by anion exchange chromatography.

the whole separation was repeated in each purification in order to prevent the molybdenum from being contaminated by a similar "tailing" of the tungsten impurity into the molybdenum fraction.

Fig. 1 also shows that the molybdenum is readily separated from the bulk of the technetium. Nevertheless, during the removal of tungsten from the mixture the molybdenum is slowly moved down the column away from the technetium which has grown into it prior to the commencement of the separation; due to the short half-life of $^{99m}$Tc a small proportion (less than 5 per cent) of the equilibrium quantity will be formed away from the main technetium peak. This has the effect of broadening the technetium elution curve and, undoubtedly some technetium will accompany the molybdenum when it is removed in its turn, since it is clear that by the time all the tungsten is removed the molybdenum is near the bottom of the column.

The complete separation from technetium is therefore accomplished in a further separation in which elution with 4 M hydrochloric acid is dispensed with and the molybdenum is fed to the column in 8 M hydrochloric acid and recovered rapidly with 1 M hydrochloric acid. The separation is then completed so quickly that there is no time for a significant quantity of $^{99m}$Tc to grow into the molybdenum during the separation itself, and the molybdenum is radiochemically pure at the time it is taken from the column.

Fig. 2 shows a separation achieved under these conditions. The feed in this case was purified $^{99m}$Tc to which a small amount of $^{99}$Mo had been added.

(b) *Purification and aliquotting*. "Deacidite" FF (<200 mesh, average cross-linking 7·9 per cent supplied by the Permutit Co. Ltd.) anion-exchange resin was washed with 2 M hydrochloric acid,

water, acetone and finally with ether, dried by blowing warm air through it and stored in a glass bottle with a tightly fitting stopper.

Each column container consisted of a piece of capillary tubing, 5 cm long and 3 mm in internal diameter, drawn out to a fine tip at one end and sealed on to another piece of glass tubing 10 cm long and 1 cm in internal diameter at the other end. A small plug of silica wool was packed into the end of the capillary and 100 mg dry resin were weighed out and slurried into the container with water. The column was washed with 1 ml 8 M hydrochloric acid and was then ready for use. Compressed air, controlled by a needle valve and manometer, was applied to the top of the column to maintain the correct flow-rate of liquid through it.

The sample was allowed to "cool" at least 3 hr after irradiation to allow the $^{101}$Mo($T_{\frac{1}{2}}$ = 14·6 min)

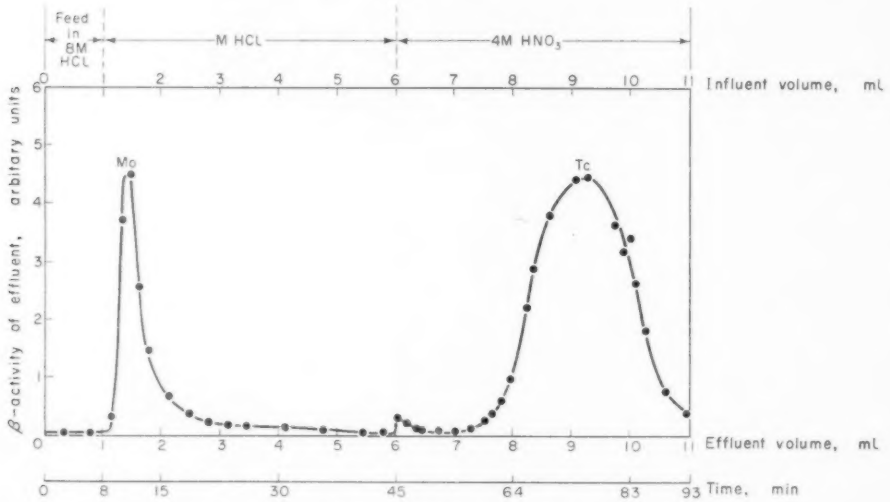



FIG. 2.—Separation of $^{99}$Mo and $^{99}$Tc by anion exchange chromatography.

and its daughter $^{101}$Tc ($T_{\frac{1}{2}}$ = 14·0 min) to decay. The ampoule was then opened, its contents were diluted to 1 ml with 8 M hydrochloric acid, a drop of concentrated nitric acid was added, and then the solution was warmed and fed to the column at a flow-rate of four drops per minute. The column was next eluted with 5 ml 4 M hydrochloric acid at the same flow-rate, the tungsten was removed in the effluent and rejected, and finally the molybdenum was recovered by elution with 2 ml M hydrochloric acid.

The solution was next evaporated to dryness; 1 ml 8 M hydrochloric acid was added to dissolve the residue, then one drop of concentrated nitric acid, and the solution warmed and fed to another 100 mg column for the process to be repeated.

Upon recovery the molybdenum was treated in the same way as before and fed to another 100 mg column. This time, when the feed was completed, the column was eluted directly with 2 ml M hydrochloric acid and the time at which the peak of the elution curve came off the column was carefully noted. This time was taken to be that at which the whole of the molybdenum could be considered to be pure and could be determined with a precision of plus or minus 1 min.

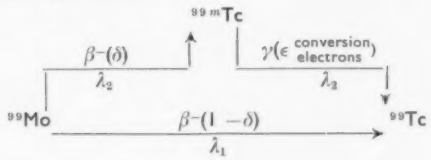
After recovery from this last column the solution was evaporated to dryness, the residue was heated to 400°, cooled and dissolved in 2 ml 3 M ammonium hydroxide. After mixing, two aliquots were taken from the resulting solution with calibrated micropipettes.

The first aliquot ($V_D \simeq 50$ $\mu$l) was pipetted onto a clear VYNS film (approximately 10 $\mu$g cm$^{-2}$) and evaporated to dryness. When dry, a second VYNS film (made conducting by evaporation on to it of about 50 $\mu$g cm$^{-2}$ gold) was made to adhere to the front of the first and the composite film was placed in the counter. In this way the source could be made ready for absolute disintegration-rate determinations within an hour of the time the molybdenum was pure.

The second aliquot (1 ml) was mixed with an equal volume of dilute ammonium hydroxide containing a known quantity of enriched $^{100}$Mo (see section on "mass spectrometric measurements"). An aliquot of the mixture was then taken for determination of its $^{98}$Mo to $^{100}$Mo ratio.

4. *Absolute disintegration rate determinations*

(a) *The mathematics of the decay of* $^{99}$Mo. The disintegration of an initially pure source of $^{99}$Mo can be simplified to the following scheme:




and it can be shown that the observed $\beta$ + conversion electron disintegration rate, $A_t$, of an initially pure source of $^{99}$Mo at time $t$ afterwards is given by the expression:

$$A_t = A_0(x + ky) \tag{1}$$

where $A_0$ = initial disintegration rate of the pure $^{99}$Mo

$x = \exp(-\lambda_1 t)$

$y = [\exp(-\lambda_1 t) - \exp(-\lambda_2 t)]$

and $k = \delta\epsilon\lambda_2/(\lambda_2 - \lambda_1)$

$\lambda_1$ and $\lambda_2$ being the radioactive decay constants of $^{99}$Mo and $^{99m}$Tc respectively, $\delta$ being the proportion of all $^{99}$Mo disintegrations which decay to $^{99}$Tc by way of $^{99m}$Tc and $\epsilon$ being the proportion of $^{99m}$Tc disintegrations which give rise to a conversion electron which is recorded by the counter.

$\lambda_1 = 0{\cdot}010502 \pm 0{\cdot}000025$ hr$^{-1}$ [8] and $\lambda_2 = 0{\cdot}1148 \pm 0{\cdot}0005$ hr$^{-1}$ [9]; both are known precisely but $\delta$ and $\epsilon$ are not. The best evidence[10] suggests $\delta$ is about 0·87. On the other hand 99 per cent of all $^{99m}$Tc atoms decay by emission of a 2 keV $\gamma$-photon (internal conversion coefficient very large) followed by a 140 keV $\gamma$-photon (internal conversion coefficient about 0·11) and the other 1 per cent give rise to a 142 keV $\gamma$-photon. The apparent value of $\epsilon$ observed in practice therefore will be critically dependent on the thickness of the source and source mount and may be expected to vary between about 0·11 for fairly thin sources to a theoretical limit of 1·0 for infinitely thin sources according to the number of conversion electrons which are detected. The constant $k$ of equation (1) cannot therefore be assumed to be the same for all sources but must be determined for each individual source.

Dividing both sides of equation (1) by $x$ we have:

$$\frac{A_t}{x} = A_0 + \frac{y}{x} \times kA_0 \tag{2}$$

A plot with $A_t/x$ as ordinate and $y/x$ as abscissa will therefore give a straight line of slope $kA_0$ which intersects the $y$-axis at $A_0$.

Fig. 3 shows such a plot from which $A_0$ was found to be 1329·8 counts/sec, $k = 0{\cdot}1409$ and hence $\delta\epsilon = 0{\cdot}128$ or $\epsilon = 0{\cdot}15$. Values of $k$ found in practice varied between 0·101 and 0·184.

(b) *Counting procedure.* As soon as it had been prepared, the source for the disintegration rate determination was placed in a $4\pi$, argon-methane-flow, proportional counter whose anode potential was adjusted for $\beta$-particle detection. Ten minute counts were taken every half-hour for the next 5 hr and the results (each corrected for background activity and paralysis losses corresponding to a dead-time of 1·2 $\mu$sec) were plotted, as illustrated in Fig. 3, to obtain $A_0$. The disintegration rate the $^{99}$Mo in the source would have had at the end of the irradiation ($A_t$) was then obtained from $A_0$.

(c) *Validity of the counting procedure.* The validity of the procedure used to determine $A_0$ depends upon the fulfilment of two conditions, i.e. (a) that the counter records all $^{99}$Mo disintegrations occurring within the source and (b) that the source is radiochemically pure.

[8] S. R. Gunn, H. G. Hicks, H. B. Levy and P. C. Stevenson, *Phys. Rev.* **107**, 1642 (1957).
[9] K. T. Bainbridge, M. Goldhaber and E. Wilson, *Phys. Rev.* **90**, 430 (1953).
[10] D. Strominger, J. M. Hollander and G. T. Seaborg, *Rev. Mod. Phys.* **30**, 586 (1958).

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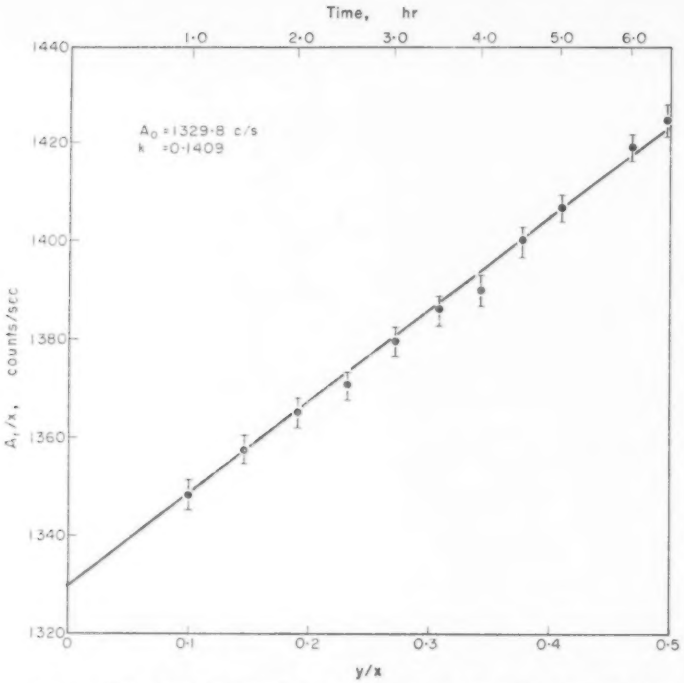


FIG. 3.—The change in counting rate of an initially pure $^{99}$Mo source with time.

$^{99}$Mo decays with the emission of $\beta$-particles of energies 1·18 (83%), 0·80 (3%) and 0·41 (14%) MeV[10] and it has been shown elsewhere[11,12] that losses due to absorption in the source mount are negligible under these conditions. The superficial density of the sources was about 2 $\mu$g cm$^{-2}$ however. Taking these facts and the mode of preparation of the sources into account, it was deduced from the work of MERRITT *et al.*[13] that losses due to self-absorption in the source may be as high as 1 per cent.

The sources were found to be extremely pure; their decay has been followed for as long as fourteen half-lives and no departure from that described by expression (1) has been found within the limits of experimental error within that time. Residual long-lived activity was less than 0·001 per cent of the initial count.

5. *Flux measurements*

These have been described elsewhere.[7]

6. *Mass spectrometric measurements*

For each mass spectrometric measurement a sample containing 2 $\mu$g or more of molybdenum was evaporated to dryness on a single tantalum filament (0·3 in. × 0·03 in. × 0·001 in.) and examined in an A.E.I. Type M.S.5 solid source mass spectrometer at a filament current of 3·8 A to 4·8 A.

A solution of natural molybdenum containing 25·02 ± 0·02 $\mu$g per ml was prepared by igniting Johnson Matthey's spectrographically pure molybdenum trioxide for 1 hr at 550°, cooling *in vacuo*, and dissolving the appropriate amount in 2 M ammonium hydroxide. A solution of similar concentration of enriched $^{100}$Mo was also prepared from 10 mg of enriched $^{100}$Mo in the form of molybdenum trioxide (supplied by the Electromagnetic Separation Group of Chemistry Division). 20 ml aliquots from each solution were taken with the same calibrated pipette and mixed together and samples from the mixtures were examined in the mass spectrometer for their $^{98}$Mo to $^{100}$Mo ratios. A similar sample of enriched $^{100}$Mo was taken for a complete isotopic analysis.

[11] M. J. CABELL, *Canad. J. Phys.* **36**, 989 (1958).
[12] M. J. CABELL, T. A. EASTWOOD and P. J. CAMPION, *J. Nucl. Energy* **7**, 81 (1958).
[13] J. S. MERRITT, J. G. V. TAYLOR and P. J. CAMPION, *Canad. J. Chem.* **37**, 1109 (1959).

The results showed the enriched $^{100}$Mo contained 85·51 ± 0·12 atom per cent $^{100}$Mo and 5·54 ± 0·04 atom per cent $^{98}$Mo.

The relationship:

$$N_{98,100} = N_{98,\text{nat}}(1 - R_M/R_{\text{nat}})/(R_M/R_{100} - 1) \quad (3)$$

in which $N_{98,\text{nat}} = y \times A_{98,\text{nat}} \times (6{\cdot}023) \times 10^{17}/(\text{A.W.})_{\text{nat}}$ was applied. $(\text{A.W.})_{\text{nat}}$, $A_{98,\text{nat}}$ and $y$ are the atomic weight of natural molybdenum, the atomic proportion of $^{98}$Mo atoms in natural molybdenum (0·239 ± 0·002) and the weight of natural molybdenum in $\mu$g per ml of unmixed solution; $N_{98,\text{nat}}$ and $N_{98,100}$ are the numbers of $^{98}$Mo atoms per ml of the unmixed solutions of natural molybdenum and enriched $^{100}$Mo respectively and $R_{\text{nat}}$, $R_{100}$ and $R_M$ are the ratios of the numbers of $^{98}$Mo to $^{100}$Mo atoms in natural molybdenum (2·48 ± 0·04), the enriched $^{100}$Mo (0·06475 ± 0·00005) and the mixtures of the two (0·3602 ± 0·0004) respectively.

One millilitre aliquots of the experimental solutions were mixed with an equal volume of the enriched $^{100}$Mo solution, taken with the same pipette, as described in the section on "purification and aliquotting". The ratio of the numbers of $^{98}$Mo atoms to $^{100}$Mo atoms in the mixtures ($R_M$*) were determined and from these results the numbers of atoms of irradiated $^{98}$Mo in the sources used for $\beta$-disintegration rate determinations ($N_0$) were calculated.

The relationship is

$$N_0 = V_D \times N_{98,100} \times (R_M^*/R_{100} - 1)/(1 - R_M^*/R_{98}) \quad (4)$$

in which $R_{98}$ is the ratio of $^{98}$Mo to $^{100}$Mo atoms in the enriched $^{98}$Mo (94·25 ± 0·11).

By this procedure $N_0$ is related directly to the $^{98}$Mo content of natural molybdenum and errors due to mass discrimination in the mass spectrometer are eliminated. It was also arranged that $R_M$* approximated to $\sqrt{R_{98}R_{100}} = 2{\cdot}5$ and that $R_M$ approximated to $\sqrt{R_{100}R_{\text{nat}}} = 0{\cdot}4$ in order to minimize the effect of random errors in $R_M$* and $R_M$ on $N_0$ and $N_{98,100}$ respectively.

A further mass spectrometric measurement was carried out on a small sample of enriched $^{100}$Mo (≏1 $\mu$g) which was put through the purification process to see if any natural molybdenum contamination was picked up from the reagents used. The results showed that the error introduced into $N_0$ due to this possible process was less than 0·02 per cent.

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## RESULTS

The cross-section results were calculated as described by EASTWOOD *et al.*[14] Following the WESTCOTT convention[15] the equilibrium reaction rate ($R_E$) for the conversion of $^{98}$Mo to $^{99}$Mo is given by the expression:

$$R_E = A_I/N_0\,(1 - \exp(-\lambda_1 t_1)) = (nv_0)_0 \quad (5)$$

in which $t_1$ is the time of irradiation, $(nv_0)$ is the 2200 m/sec flux and $\hat{\sigma}$ is the effective cross-section for $^{98}$Mo in the reactor spectrum chosen. The 2200 m/sec flux and $r\sqrt{(T/T_0)}$ are determined from the monitor measurements, $s_0$ is determined from the ratio of $R_E$ for unshielded and cadmium-shielded $^{98}$Mo ($R_{\text{Cd,Mo}}$) and $\hat{\sigma}$ is related to $\sigma_0$, the 2200 m/sec cross-section, by the expression:

$$\hat{\sigma} = \sigma_0\,(1 + {}^{r}\sqrt{(T/T_0)}s_0) \quad (6)$$

The resonance integral $(\text{R.I.})_{\text{Mo}}$, from a lower cut-off of 0·5 eV (for 0·068 cm cadmium) to fission energies, is given by the expression:

$$(\text{R.I.})_{\text{Mo}} = (\text{R.I.})_{\text{Au}} \cdot \sigma_{0,\text{Mo}} \cdot (R_{\text{Cd}} - 1)_{\text{Au}}/\sigma_{0,\text{Au}} \cdot (R_{\text{Cd}} - 1)_{\text{Mo}} \quad (7)$$

Table 1 shows a complete series of results for a pair of experiments.

Table 2 provides a summary of all the cross-section results.

[14] T. A. EASTWOOD, A. P. BAERG, C. B. BIGHAM, F. BROWN, M. J. CABELL, W. E. GRUMMITT, J. C. ROY and R. P. SCHUMAN, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva* (1958) P/203. United Nations (1959).

[15] C. H. WESTCOTT and T. K. ALEXANDER. *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva* 1958, P/202. United Nations (1959).

TABLE 1.—COMPLETE RESULTS FOR A PAIR OF EXPERIMENTS

| Experiment number | 3 (without cadmium cover) | 4 (with cadmium cover) |
|---|---|---|
| $t_1$ (hr) | 6·900 ± 0·001 | 6·900 ± 0·001 |
| $A_I$ (disintegrations/sec.) | 213·8 ± 1·3 | 128·0 ± 1·1 |
| $V_D$ ($\mu$l) | 50·06 ± 0·10 | 50·06 ± 0·10 |
| $R_M$* | 2·321 ± 0·044 | 2·186 ± 0·102 |
| $N_0$ | (1·256 ± 0·025) . $10^{16}$ | (1·179 ± 0·054) . $10^{16}$ |
| $R_E(^{98}Mo)$ (sec$^{-1}$) | (2·435 ± 0·053) . $10^{-13}$ | (1·553 ± 0·073) . $10^{-13}$ |
| $R_E(^{197}Au)$ (sec$^{-1}$) | (9·87 ± 0·08) . $10^{-11}$ | (3·56 ± 0·03) . $10^{-11}$ |
| $r\sqrt{(T/T_0)}$ | 0·0315 ± 0·0004 | |
| $\hat{\sigma}_{Au}$ (barns) | 153·5 ± 0·7 | |
| $(nv_0)$ neutrons cm$^{-2}$ sec$^{-1}$. | (6·43 ± 0·06) × $10^{11}$ | |
| $\hat{\sigma}_{Mo}$ (barns) | 0·379 ± 0·010 | |
| $R_{Cd}(^{98}Mo)$ | 1·57 ± 0·08 | |
| $s_0(^{98}Mo)$ | 54·8 ± 7·9 | |
| $\hat{\sigma}_0(^{98}Mo)$ (barns) | 0·134 ± 0·004 | |
| $(R.I.)_{Mo}$ (barns) | 6·60 ± 0·32 | |

TABLE 2.—$^{98}$Mo CROSS-SECTION RESULTS

| Experiments | $t_1$ (hr) | $\hat{\sigma}$ (barns) | $\sigma_0$ (barns) | (R.I.) (barns) |
|---|---|---|---|---|
| 1 and 2 | 12·000 | 0·389 ± 0·012 | 0·138 ± 0·005 | 7·13 ± 0·15 |
| 3 and 4 | 6·900 | 0·379 ± 0·010 | 0·134 ± 0·004 | 6·60 ± 0·32 |
| 5 and 6 | 4·000 | 0·365 ± 0·008 | 0·132 ± 0·004 | 6·55 ± 0·22 |
| 6 and 7 | 4·000 | 0·372 ± 0·010 | 0·140 ± 0·005 | |
| 8 and 9 | 5·000 | 0·391 ± 0·012 | 0·137 ± 0·005 | 6·77 ± 0·14 |
| 9 and 10 | 5·000 | 0·380 ± 0·006 | 0·127 ± 0·005 | |
| 11 and 12 | 9·000 | 0·376 ± 0·008 | 0·139 ± 0·003 | 6·46 ± 0·11 |
| Weighed average | | 0·377 ± 0·004 | 0·136 ± 0·001 | 6·69 ± 0·09 |

## CONCLUSIONS

In both Tables 1 and 2 the errors expressed are all random in origin (errors in pipetting, statistical errors in counting, errors in weighing the monitors and errors in $R_M$*, of which the last is the most important) and are twice the standard deviation in each case. A weighted mean of the results gives $\hat{\sigma} = 0{\cdot}377 \pm 0{\cdot}004$ barns, $\sigma_0 = 0{\cdot}136 \pm 0{\cdot}001$ barns and (R.I.) $= 6{\cdot}69 \pm 0{\cdot}09$ barns where the error quoted is the probable error of the mean in each case. Making allowance for systematic errors also (possible counting losses in determining absolute disintegration rates, errors in $R_M$, $A_{98,nat}$ and pipette calibrations etc.) the final results obtained were $\hat{\sigma} = 0{\cdot}377 \pm 0{\cdot}007$ barns (for $r\sqrt{(T/T_0)} = 0{\cdot}032$), $\sigma_0 = 0{\cdot}136 \pm 0{\cdot}003$ barns and (R.I.) $= 6{\cdot}69 \pm 0{\cdot}13$ barns.

The result obtained for $\hat{\sigma}$ is not inconsistent with that quoted by SEREN *et al.*[2] and that for $\sigma_0$ is in good agreement with the value quoted in A.E.C.U. 2040[4]; it does not agree however with the later B.N.L. 325 values.[5,6] It is not possible to say why this discrepancy exists because the experimental details for the last work has not been published. No resonance integral data have been published before.

*Acknowledgements*—Grateful acknowledgement is made to Mr. D. MAPPER for his help with the $\gamma$-spectrometric measurements and to Mr. L. J. SLEE for some of the mass spectrometric measurements.

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# CALCULATED FORMATION CROSS-SECTIONS OF $Ca^{45}$ AND $Ca^{47}$

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**Abstract**—The formation cross-sections of $^{45}Ca$ and $^{47}Ca$ as a function of bombarding energy are computed. The nuclear reactions considered are the bombardment of $^{48}Ti$ and $^{50}Ti$ with neutrons and deuterons and the bombardment of $^{48}Ca$ with neutrons, protons, deuterons, $^{3}He$ and $^{4}He$ particles. The calculations assume the formation of an excited compound nucleus with the subsequent de-excitation through nuclear evaporation. The effect of various assumptions is discussed. It is concluded that for the purpose of large scale production of $^{47}Ca$, the $^{48}Ca(n, 2n)^{47}Ca$ reaction is by far the most useful of all reactions considered.

THE radioactive isotopes of calcium, $^{45}Ca$ and $^{47}Ca$ (half-life: 160 days and 4·7 days respectively) are of considerable importance for tracer work in biological systems. It is, therefore, of interest to have a theoretical estimate of the formation cross-section of these isotopes as a result of the bombardment of neighbouring stable nuclides with medium energy neutrons and charged particles. Table 1 shows the reactions which are considered here. The calculations are based on the assumption of compound nucleus formation of the target and incoming particle, with the subsequent evaporation of one or more particles. The Monte-Carlo programme which has been used for these calculations has been described elsewhere.[1,2] The following parameters were used: (a) The nuclear radius parameter $r_0 = 1{\cdot}7 \times 10^{-13}$ cm. (b) The nuclear level density parameter $a = A/20$ MeV$^{-1}$. (c) The semiempirical values for the pairing energies published by CAMERON.[3] (d) The shell energy correction $\delta_s = 1{\cdot}0$ MeV.

TABLE 1.—EXCITATION FUNCTIONS COMPUTED IN THIS PAPER

| Target nucleus | Compound nucleus | Reaction | Product |
|---|---|---|---|
| $^{48}_{22}Ti$ | $^{49}_{22}Ti$ | $(n, \alpha)$ | $^{45}_{20}Ca$ |
| $^{48}_{22}Ti$ | $^{50}_{23}V$ | $(d, p\alpha)$ | $^{45}_{20}Ca$ |
| $^{50}_{22}Ti$ | $^{51}_{22}Ti$ | $(n, \alpha)$ | $^{47}_{20}Ca$ |
| $^{50}_{22}Ti$ | $^{52}_{23}V$ | $(d, p\alpha)$ | $^{47}_{20}Ca$ |
| $^{48}_{20}Ca$ | $^{49}_{20}Ca$ | $(n, 2n)$ | $^{47}_{20}Ca$ |
| $^{48}_{20}Ca$ | $^{49}_{21}Sc$ | $(p, pn)$ | $^{47}_{20}Ca$ |
| $^{48}_{20}Ca$ | $^{50}_{21}Sc$ | $(d, p2n)$ | $^{47}_{20}Ca$ |
| $^{48}_{20}Ca$ | $^{51}_{22}Ti$ | $(^3He, \alpha)$ | $^{47}_{20}Ca$ |
| $^{48}_{20}Ca$ | $^{52}_{22}Ti$ | $(\alpha, \alpha n)$ | $^{47}_{20}Ca$ |

[1] I. DOSTROVSKY, P. RABINOWITZ and R. BIVINS, *Phys. Rev.* **111**, 1659 (1958).
[2] I. DOSTROVSKY, Z. FRAENKEL and G. FRIEDLANDER, *Phys. Rev.* **116**, 683 (1959).
[3] A. G. W. CAMERON, *Canad. J. Phys.* **36**, 1040 (1958).

The same shell energy correction was used for both the $Z = 20$ and the $N = 28$ shells. Thus the total *shell* correction for the doubly magic $^{48}Ca$ was 2·0 MeV in addition to the total *pairing* energy correction of 2·98 MeV[3].

The calculated excitation curves are shown in Figs. 1–3. An estimate of the statistical accuracy of the cross-section may be obtained from the curve of the $^{48}Ca(n, 2n)^{47}Ca$ reactions where the statistical errors are indicated. No experimental values have been published for any of these reactions and this makes it difficult to estimate the accuracy of the calculations. However, based on previous comparisons

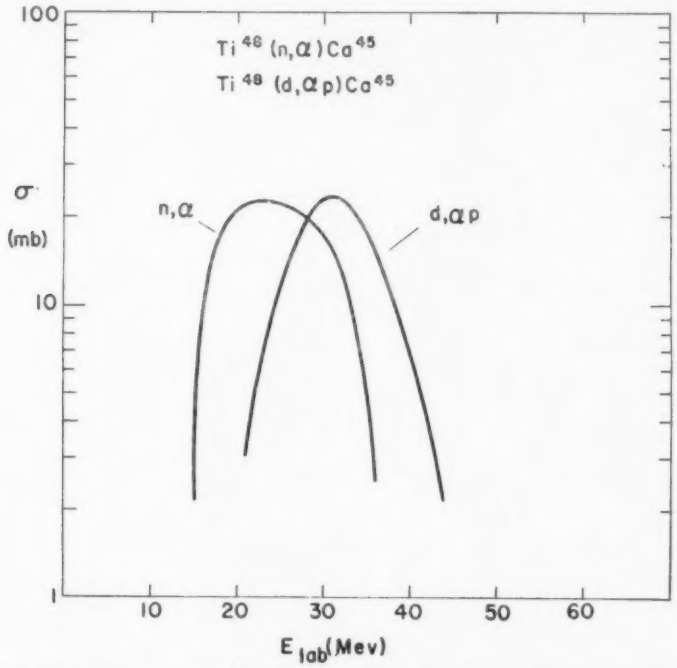


FIG. 1.—Excitation functions of $^{45}Ca$ from the bombardment of $^{48}Ti$ with neutrons and deuterons.

of calculated and experimental values for this mass region it is believed that the maximum values of the $(p, pn)$ and $(d, p2n)$ reactions on $^{48}Ca$ are probably in error by less than a factor of two. The error is presumably considerably smaller for the $(n, 2n)$ reaction, but it may be larger for the other reactions. On the other hand, due to an approximation in the calculation which has been discussed in detail,[2] the curves may be shifted somewhat towards higher bombarding energies. The shift is probably less than 2·5 MeV (which is approximately the total shell and pairing correction of the residual nuclei $^{45}Ca$ and $^{47}Ca$).

Another factor which will affect the accuracy of the calculated excitation curves are direct interactions. These reactions compete with the compound nucleus formation process, with the result that the actual compound nucleus cross-section is smaller than the calculated one. The calculated excitation curves which are based on the assumption of no such competition will, therefore, in general be found to be an overestimate. The effect of the direct interactions on the total reaction cross sections shown here is

quite small up to a bombarding energy of approximately 30 MeV. But at a bombarding energy of about 50 MeV the direct interactions account already for 60–70 per cent of the total reaction cross-section.[4] Hence the reactions $(d, \alpha p)$, $(d, p2n)$ and $(\alpha, \alpha n)$ might be expected to fall off much *more* rapidly than indicated in Figs. 1–3. The reactions $(n, 2n)$ and $(p, pn)$ which proceed also through direct interactions, the $(p, pn)$ reaction being a typical pick-up reaction, will fall off much *less* rapidly than indicated by the calculations.

It may perhaps be useful to make some general comments on the relative position

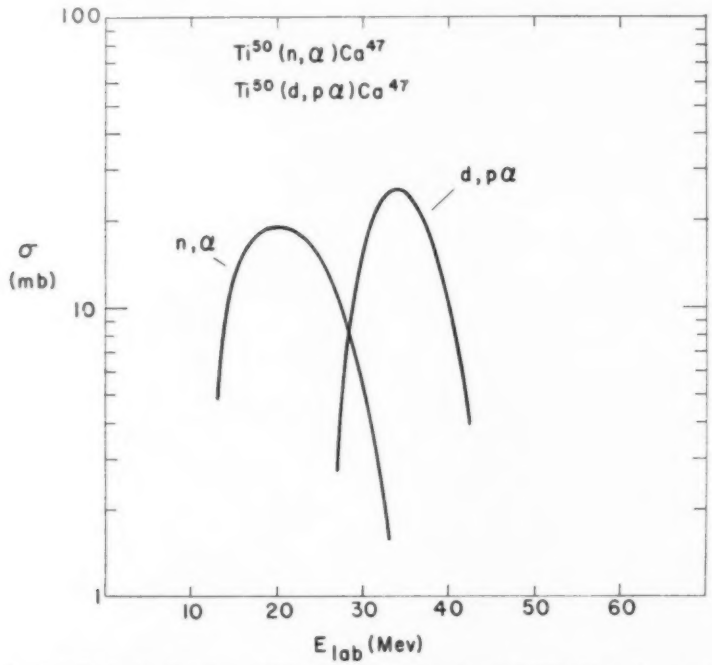


FIG. 2.—Excitation functions of $^{47}$Ca from the bombardment of $^{50}$Ti with neutrons and deuterons.

and the shape of the excitation curves. The notation for the reactions is intended to indicate the final product only, not the reaction path. Thus the cross-section for the $^{48}$Ca$(p, pn)^{47}$Ca reaction includes also the $(p, np)$ and the $(p, d)$ reactions. The peak of all reaction in which only one particle is emitted is at approximately the same excitation energy of the compound nucleus. The same is true for the reactions which proceed primarily through the emission of two particles. The difference in the peak positions shown in Figs. 1–3 is due to the difference in the $Q$-value of the bombarding particle. This difference causes also to some extent the large difference in maximum cross-section for these reactions. For example the large $Q$-value of the $^{48}$Ca + $^{3}$He reaction causes the peak of the $^{48}$Ca($^{3}$He, $\alpha$) reaction to be shifted to a low bombarding energy. At this energy the capture cross section of the $^{3}$He is quite low (0·7 mbarns) due to the high Coulomb barrier (approximately 6 MeV) of the $^{3}$He particle. Because

[4] N. METROPOLIS, R. BIVINS, M. STORM, A. TURKEVICH, J. M. MILLER and G. FRIEDLANDER, *Phys. Rev.* **110**, 185 (1958).

of this reason the maximum cross section of the ($^3$He, $\alpha$) reaction is smaller by a factor of ten than that of the ($\alpha$, $\alpha n$) reaction despite the fact that the latter reaction involves the emission of two particles. The large number of reaction paths through which some of the reactions can proceed is well illustrated by the shape of the $^{48}$Ca($\alpha$, $\alpha n$)$^{47}$Ca

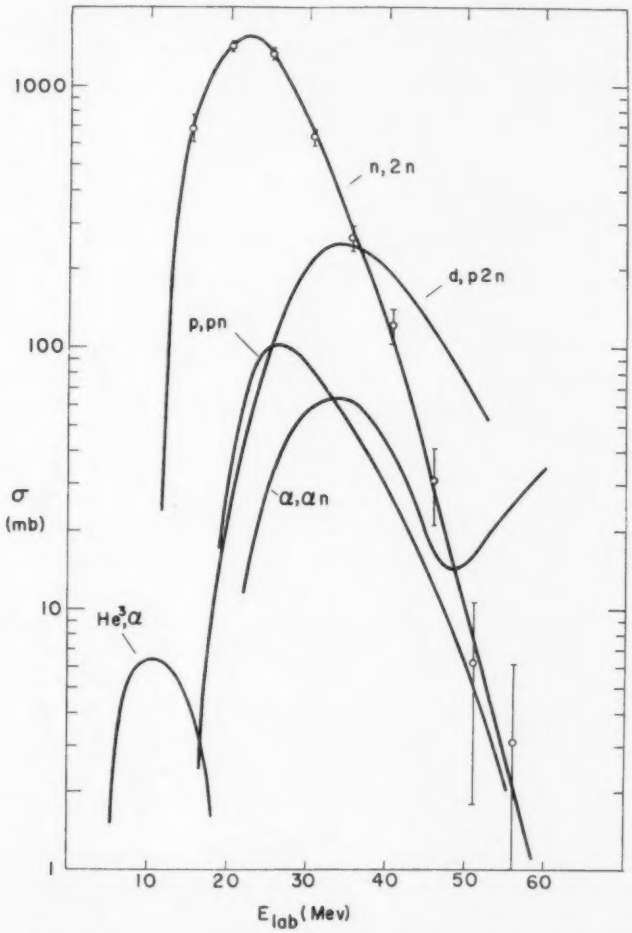


FIG. 3.—Excitation functions of $^{47}$Ca from the bombardment of $^{48}$Ca with neutrons, protons, deutrons, $^3$He and $^4$He particles.

excitation curve. This reaction proceeds predominantly through the reaction paths ($\alpha$, $\alpha n$) and ($\alpha$, $n\alpha$) up to a bombarding energy of approximately 50 MeV. Beyond this energy the cross-section for these reaction paths continues to fall off but the reactions involving the mission of three or more particles like ($\alpha$, *ddn*), ($\alpha$, *dp2n*) and ($\alpha$, 2*p* 3*n*) cause the excitation curve to rise again. It should be noted that because of the large competition of direct interactions at these energies, this renewed rise of the excitation curves is probably not discernible by experiment and certainly of no practical value for the production of the $^{47}$Ca isotope.

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From Figs. 1–3 it is readily seen that if one is interested in the large scale production of $^{47}$Ca with as little a contamination of $^{45}$Ca as possible, the $^{48}$Ca($n$, $2n$)$^{47}$Ca reaction is by far the most useful one of all reactions considered (see Fig. 3). Not only has this reaction a maximum cross section of over 1·5 barns, but this maximum is also at an energy which is within the range of all Van der Graaff machines capable of accelerating deuterons to an energy above 3 MeV. (Neutron production through the reaction $d$($^3$H, $\alpha$)$n$ is here assumed.) Since the cross-section of the above reaction is quite high (approximately 400 mbarns) even at a neutron energy of 14 MeV, electrostatic accelerators (Cockroft-Walton) capable of producing 0·5 MeV deuterons could also be used successfully for the production of $^{47}$Ca from $^{48}$Ca. Moreover since the natural abundance of $^{48}$Ca is more than fifty times that of $^{46}$Ca, the contamination of $^{45}$Ca will be very small. The main disadvantage of using this reaction for the production of $^{47}$Ca is the low abundance of $^{48}$Ca and hence its high price.

Another reaction which may be used is the $^{50}$Ti($n$, $\alpha$)$^{47}$Ca reaction (Fig. 2). The maximum cross-section of this reaction is almost by a factor of 100 smaller than that of the $^{48}$Ca($n$, $2n$)$^{47}$Ca reaction. However the isotope $^{50}$Ti is much more abundant than $^{48}$Ca and hence cheaper. Since the $^{48}$Ti($n$, $\alpha$)$^{45}$Ca excitation curve is similar to the $^{50}$Ti($n$, $\alpha$)$^{45}$Ca and also has the peak at the same neutron energy, the degree of purity of the $^{50}$Ti (with respect to $^{48}$Ti) would have to be quite high.

The reactions involving deuterons as bombarding particles, $^{50}$Ti($d$, $p\alpha$)$^{47}$Ca and $^{48}$Ca($d$, $p2n$)$^{47}$Ca, though having fairly large cross-sections, suffer from the disadvantage that the maximum cross-section is obtained only at a bombarding energy of 35 MeV, above the range of most present day high current machines. Moreover, it has already been pointed out that due to competition of stripping, all reactions involving deuterons as bombarding particles shown in Figs. 1–3 have actually a considerably lower cross-section than indicated by the curves.

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# RANGES OF FISSION FRAGMENTS IN GASES—I

## RANGES IN AIR OF FRAGMENTS FROM SPONTANEOUS FISSION OF $^{252}Cf$*

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(*Received* 28 *February* 1961)

**Abstract**—Differential ranges in air have been measured for nineteen fission products of known mass resulting from the spontaneous fission of $^{252}Cf$. A comparison is made with the measured fission fragment ranges from $^{239}Pu$ and a kinetic energy-range correlation obtained.

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THE only previous differential measurements of the ranges of fission fragments of known mass in air are those of KATCOFF, MISKEL and STANLEY on fragments produced by neutron irradiation of $^{239}Pu$.[1] The pronounced dip observed in the range-vs.-mass curve in the region corresponding to symmetric fission seemed interesting enough to warrant further investigation of this region using different fissioning nuclides.

Since the process of spontaneous fission might be expected to be different from neutron-induced fission, the present work was undertaken to measure the ranges of the fragments produced by spontaneous fission of $^{252}Cf$.

### EXPERIMENTAL

The apparatus for the collection of the fission fragments is shown schematically in Fig. 1. In use, a source of ~1 $\mu$g of $^{252}Cf$, electro-deposited in a 1 cm diameter circle on a platinum backing, was placed at one end of the cylindrical chamber and a series of 0·125 in. spacer rings was placed coaxially

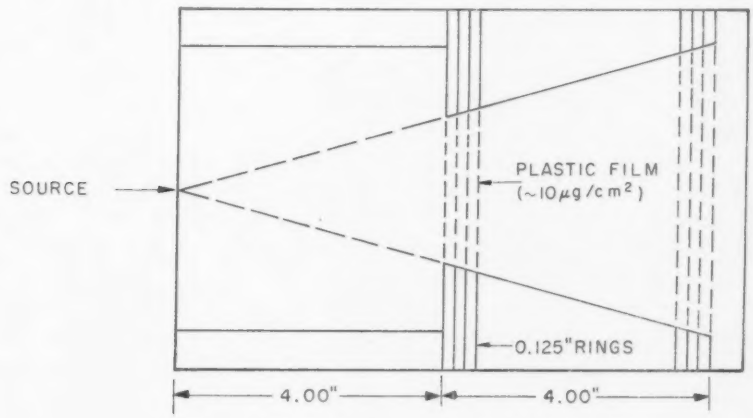


FIG. 1.—Fission-fragment range chamber.

* This work was performed under the auspices of the U.S. Atomic Energy Commission.

[1] S. KATCOFF, J. A. MISKEL and C. W. STANLEY, *Phys. Rev.* **74**, 631 (1948). Note that the ranges reported in this paper are at 15°C.

with, and began 4·00 in. from, the source. Each ring supported a film of VYNS (a polyvinylchloride-acetate copolymer) of the order of 10 $\mu$g/cm.* The thickness of each film was determined on a Cary spectrophotometer at a wavelength of 360 m$\mu$. The instrument was calibrated by measurement of the transmission of several films of known weight and area.[2]

Due to the low fission rate of the Cf source ($\sim 10^7$ fission/min) the activity of a specific fission product on a single film was quite low. For this reason the collection apparatus was designed such that each film subtended the same solid angle. The maximum solid angle of 1 per cent was limited by the requirements that the range resolution be at least 1 per cent and that the films be self supporting.

The chamber was enclosed in an aluminum can and evacuated to a pressure of $\sim 5$ $\mu$. Dry air was then admitted until the desired pressure, as measured with a mercury manometer and vernier cathetometer, was obtained, the chamber was sealed, and the temperature recorded. Collection periods varied from several hours to a few days, depending upon the half-lives of the fission products of most interest. At the end of a run the chamber was returned to atmospheric pressure and the films removed. The first and last films were discarded, and each of the remaining films was then dissolved in fuming $H_2SO_4$–$HNO_3$. Appropriate carriers were added, and standard radio-chemical procedures were used to separate the various fission products.

After the isotopes were mounted, the decay of each was followed with an end-window $\beta$-proportional counter. The background of this counter was reduced to $\sim 2$ counts/min by means of an anticoincidence bank in conjunction with the usual lead and iron shield.

The specific activity (counts $min^{-1}$ $mg^{-1}$) on each film at the time of irradiation end was determined for each isotope by drawing a line with the known half-life through the decay points and extrapolating.

## EXPERIMENTAL RESULTS

Since particles stopping in the 4 in. between the source and the first film might drift to this film, it was always discarded. Similarly, since particles passing beyond the last film might drift back to it, this film was also discarded. The experiment was designed so that practically all stopping was in the gas, with the films contributing at most only 5 per cent. It was assumed that a particle coming to rest in the 0·125 in. space between the films would drift to the closer film or to the walls. The maximum perpendicular distance a particle would have had to drift to reach a film, assuming it stopped exactly halfway between two films, was 0·062 in., while the average perpendicular distance to the walls was about 0·3 in. Thus the number of particles lost to the walls was very small compared with the number collected. The diameter of the films was sufficiently large that a finite difference existed between that path length from the source to the centre of the film and that to the outside edge; for this reason the particles collected on a film represent a distribution of flight distances. Because a circle of radius 0·707 times the radius of the film contains half the area of the film—and half the fission fragments, assuming isotropic emission—a line drawn from the source to a point on the circumference of this circle represents the median flight distance (m.f.d.).

The specific activities were used to obtain the mean ranges of the isotopes graphically. For convenience, the specific activities were plotted vs. ring number, and only the position of the peak was converted to a m.f.d. The close and equal spacing of the films enabled three types of plots to be employed:

1. A plot on rectangular paper of specific activity vs. ring number (Fig. 2a) from which the position of the peak was estimated after drawing a smooth curve through the points.
2. A plot on rectangular paper of the difference of specific activities between

* For a detailed description of the method of preparation and measurement of the films see PATE and YAFFE.[2]

[2] B. D. PATE and L. YAFFE, *Canad. J. Chem.* **33**, 15 (1955).

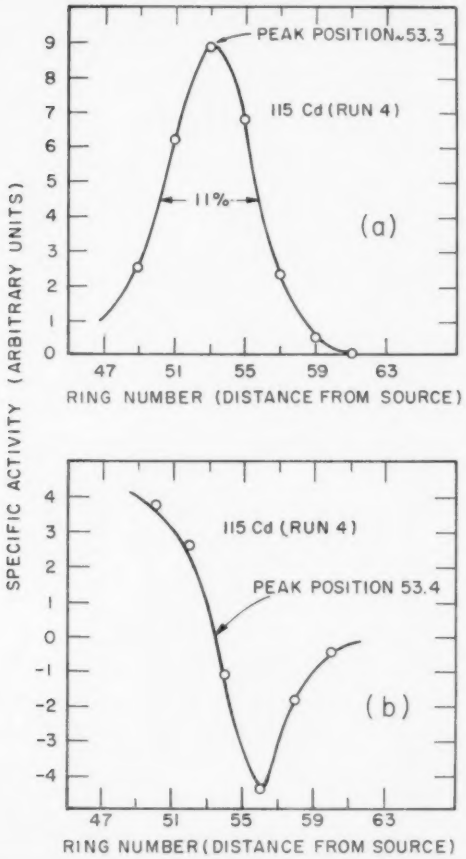


FIG. 2.—(a) Typical differential range curve, with a width 11 per cent of the total range.
(b) Typical differential range derivative curve.

successive films versus ring number (Fig. 2b). The peak was taken as the point where this difference was equal to zero. (Slope of the differential range curve equals zero.)

3. A plot on probability paper (Fig. 3) from which the peak was determined by the following method. The area under the differential range curve was proportional to the total specific activity on all films. The sum of the specific activities on those films between the ring closest to the source and any given ring (inclusive) divided by the total specific activity was proportional to the fraction of the area under the differential range curve from the first to the given ring. This fraction was plotted on probability paper vs. ring number, and the point of intersection of the resulting straight line and the 0·50 line on the paper was taken as the peak of the differential range curve.

Some error may be introduced in the peak positions as determined from the probability plots, due to the fact that the specific activities of the first and last points are not zero. This error depends on the difference between these activities, and amounts to about 0·005 cm for each mass.



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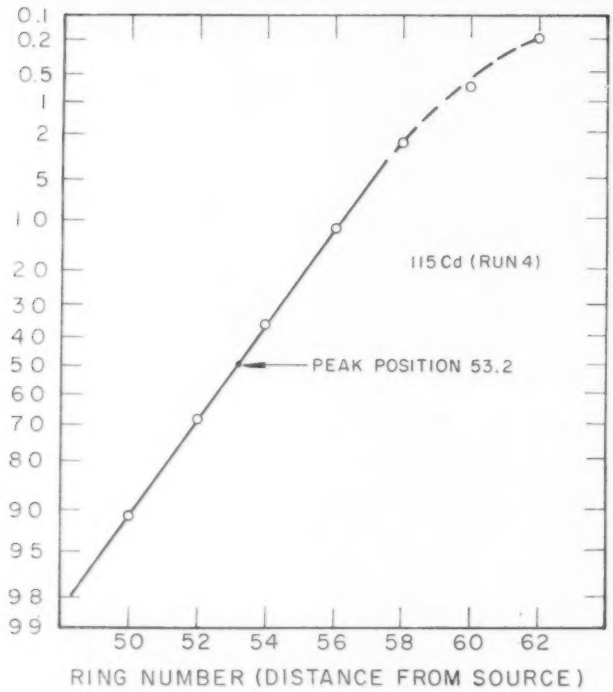


FIG. 3.—Typical probability plot for determination of the peak of the differential range curve.

TABLE 1.—MEAN RANGES OF $^{252}Cf$ FISSION FRAGMENTS IN AIR
(cm, 0°C, 760 mm)

| Isotope | Run 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | Average | Calc. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^{91}Sr$ | 2·42 | 2·44 | | | | | | | | | | | 2·43 ± 0·01 | 2·39 |
| $^{91}Y$ | | | 2·42 | | | | | | | | | | 2·42 | 2·39 |
| $^{93}Y$ | | 2·42 | 2·42 | | | | | | | | | | 2·42 | 2·39 |
| $^{97}Zr$ | | 2·38 | 2·40 | 2·33 | | | | | | | | | 2·37 ± 0·02 | 2·39 |
| $^{99}Mo$ | 2·30 | 2·34 | 2·32 | 2·33 | 2·33 | | | | | | | | 2·32 ± 0·01 | 2·38 |
| $^{111}Ag$ | 2·21 | 2·21 | | 2·21 | 2·21 | 2·21 | 2·21 | 2·21 | | | | | 2·21 ± 0·01 | 2·26 |
| $^{112}Ag$ | 2·20 | | | | 2·21 | | | | | | | | 2·20 ± 0·01 | 2·24 |
| $^{115}Cd$ | | 2·16 | | 2·18 | | | 2·14 | | | | | | 2·16 ± 0·01 | 2·18 |
| $^{121}Sn$ | | | | | | | | | 2·16 | 2·12 | | | 2·14 ± 0·02 | 2·10 |
| $^{127}Sb$ | | | | | | | | | | 2·02 | | | 2·02 | 2·06 |
| $^{132}Te$ | | | | | | | | 1·99 | 2·01 | | 1·99 | | 2·00 ± 0·01 | 2·00 |
| $^{139}Ba$ | | | | | | | | | | | | 1·93 | 1·93 | 1·88 |
| $^{140}Ba$ | | | | | | | | | | | | 1·90 | 1·90 | 1·88 |
| $^{141}Ce$ | | | | | | | | 1·91 | | | 1·86 | | 1·88 ± 0·02 | 1·86 |
| $^{143}Ce$ | | | | | | | | 1·90 | | | 1·82 | | 1·86 ± 0·04 | 1·83 |
| $^{147}Nd$ | | | | | | | | 1·86 | | 1·85 | | | 1·86 ± 0·01 | 1·80 |
| $^{153}Sm$ | | | | | | | | 1·81 | | 1·80 | | | 1·80 ± 0·01 | 1·76 |
| $^{156}Eu$ | | | | | | | | 1·77 | | 1·79 | | | 1·78 ± 0·01 | 1·74 |
| $^{161}Tb$ | | | | | | | | 1·74 | | 1·76 | | | 1·75 ± 0·01 | |

Although the curves were not perfectly Gaussian (many of them exhibited slight negative skewness), the probability plots were sufficiently straight that good results were obtained. In fact, in those cases for which all three types of plots were prepared excellent agreement was obtained for the peak position.

The mean ranges (in centimetres, corrected to 0°C and 760 mm) are given in Table 1, and plotted as a function of mass number in Fig. 4. Seven independent runs yielded an average value for the range of $^{111}$Ag of 2·21 ± 0·01 cm, and the ranges of the other isotopes except those obtained from runs 3, 9, 11, and 12 were normalized to this value.

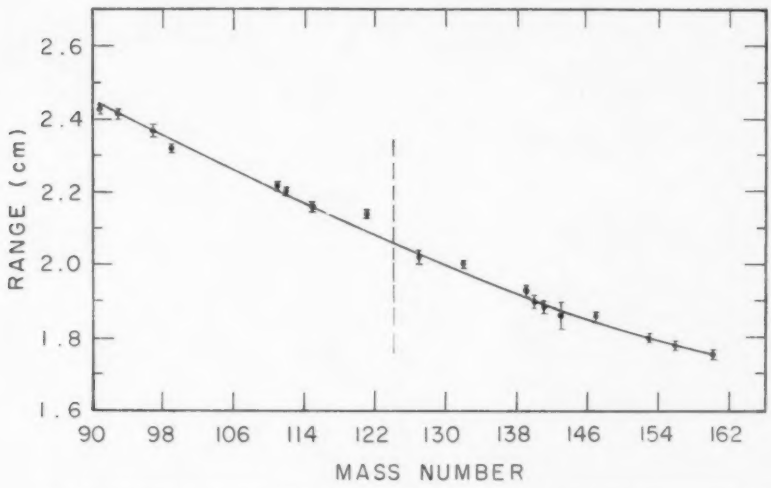


FIG. 4.—Range in air (cm, 0°C, 760 mm) for fission fragments from spontaneous fission of $^{252}$Cf. The broken line indicates symmetric fission.

Run 3 was normalized to the average value of 2·32 cm for $^{99}$Mo obtained from runs 1, 2, 4, and 5. Runs 9, 11, and 12 were absolute runs (i.e. not normalized), and it can be seen that in the cases of runs 9 and 11 good agreement with the $^{132}$Te value from run 8 (normalized) is obtained. While no direct comparison can be made for the case of run 12, the ranges measured for masses 139 and 140 are consistent with those measured for other masses in this region.

Although there is some deviation from a smooth curve, the range vs. mass-number plot (Fig. 4) does not reveal the pronounced dip in the vicinity of symmetric fission that was observed for the case of neutron-induced fission of $^{239}$Pu. This is in contradiction to the kinetic-energy data obtained from time-of-flight measurements by STEIN and WHETSTONE,[3] but is in agreement with the data of MILTON and FRASER.[4]

According to NIDAY,[5] the dip in the range-mass curve for $^{252}$Cf fission fragments would be expected to occur only over a very narrow range of mass numbers. It is therefore possible that a dip does exist between masses 121 and 127 which is not apparent from this experiment. A range measurement for mass 123 ($^{123}$Sn) or its partner mass 125 ($^{125}$Sn) would indicate this dip if it exists, but the low fission rate of the Cf source,

[3] W. E. STEIN and S. L. WHETSTONE, JR., *Phys. Rev.* **11**, 476 (1958).
[4] J. C. D. MILTON and J. S. FRASER, *Phys. Rev.* **111**, 877 (1958).
[5] J. B. NIDAY, *Phys. Rev.* **121**, 1471 (1961).

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coupled with the low fission yields and unfavorable half-lifes of these isotopes, prevented the determination from being made in this work.

BOHR[6] has derived an expression for the range, $R$, of a fission fragment as a function of its nuclear charge, $Z$, mass, $A$, and initial kinetic energy, $E$:

$$R = kA^{\frac{1}{2}}E^{\frac{1}{2}}Z^{-\frac{2}{3}}$$

where $k$ is a constant characteristic of the stopping medium. The plutonium fission-range data[1] were used in conjunction with the kinetic-energy data of STEIN[7] to calculate $k$ for air; the value of $Z$ employed was the $Z_p$ calculated from an equal charge displacement hypothesis.[8] The values of $k$ obtained were not constant and varied from 0·253 to 0·278. For this reason, a plot of $k$ vs. $Z_p$ was made. Calculations were then made of the expected ranges in air of the fission fragments from $^{252}$Cf using the kinetic energy data of MILTON and FRASER and the values of $k$ determined from the plot of $k$ vs. $Z_p$ for $^{239}$Pu. The results of this calculation are given in the last column of Table 1. The average deviation of the calculated ranges from the observed is less than 1 per cent. Similar measurements with other fissionable nuclides are in progress.

*Acknowledgements*—The authors would like to thank Drs. S. G. THOMPSON for supplying the $^{252}$Cf, R. GATTI and L. PHILLIPS for assistance in handling the source, and W. E. NERVIK for performing the rare-earth separations.

[6] N. BOHR, *Phys. Rev.* **59**, 270 (1941); *Dan. Mat. Fys.* **18**, No. 8 (1948).
[7] W. E. STEIN, *Phys. Rev.* **108**, 94 (1957).
[8] L. E. GLENDENIN, C. D. CORYELL and R. R. EDWARDS, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 489. McGraw-Hill, New York (1951).

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# THE CALCULATIONS OF STABILITY CONSTANTS USING A HIGH SPEED DIGITAL COMPUTER

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**Abstract**—A least squares technique for calculating stability constants from potentiometric titration data is described for use with a high speed digital computer such as the I.B.M. 650.

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FOR systems of metal ions and ligands which can form complexes, over a wide range of concentration several complexes may coexist in an equilibrium mixture. The relative concentrations of the complexes is dependent on the concentration of the ligand. The relationship between this latter quantity, $[L]$, and the average number of ligands complexed per metal atom, $\bar{n}$, is given by:

$$\bar{n} = \frac{\sum_{n=1}^{N} n\beta_n[L]^n}{1 + \sum_{n=1}^{N} \beta_n[L]^n} \tag{1}$$

In this equation $N$ is the maximum number of ligands which can be bound by the metal ion, and $\beta_n$ is the overall stability constant for the formation of the complex $ML_n$. $\beta_n$ is related to the stepwise formation constants by the expression

$$\beta_n = \prod_{i=1}^{n} K_i$$

By using a sufficient range of $\bar{n}$ and $[L]$ values, equation (1) can be solved algebraically[1–5] or graphically[6,7] for the constants $\beta_n$. In order to decrease the amount of time consumed in the application of either of these methods of solution, a least squares high speed digital computer technique has been developed to calculate stability constants.[8,9] Concurrently, a sequence of papers by RYDBERG and co-workers have dealt with similar computation methods for programming solvent extraction as well as potentiometric titration data[10–13]. The object of this paper is to put forth our calculation approach, with particular regard to the lanthanide complexes.

[1] J. BJERRUM, *Metal Ammine Formation in Aqueous Solution*. Hasse, Copenhagen (1941).
[2] J. C. SULLIVAN and J. C. HINDMAN, *J. Amer. Chem. Soc.* **74**, 6091 (1952).
[3] B. P. BLACK and D. H. MCINTYRE, Jr., *J. Amer. Chem. Soc.* **75**, 5667 (1953).
[4] H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.* 3397 (1953).
[5] J. Z. HERRON and J. B. GILBERT, *J. Amer. Chem. Soc.* **77**, 2594 (1955).
[6] G. SCHWARZENBACH, *Helv. Chim. Acta* **33**, 947 (1950).
[7] F. J. C. ROSSOTTI and H. S. ROSSOTTI, *Acta Chem. Scand.* **9**, 1166 (1955).
[8] G. R. CHOPPIN and J. A. CHOPOORIAN, *J. Inorg. Nucl. Chem.* In press.
[9] E. FRIEDEN and L. SPIEGEL, Paper No. 109, Division of Biochemistry, 136th meeting, American Chemical Society, Atlantic City, N.J. (1959).
[10] J. RYDBERG and J. C. SULLIVAN, *Acta Chem. Scand.* **13**, 186 (1959).
[11] J. C. SULLIVAN, J. RYDBERG and W. MILLER, *Acta Chem. Scand.* **13**, 2023 (1959).
[12] J. RYDBERG and J. C. SULLIVAN, *Acta Chem. Scand.* **13**, 2057 (1959).
[13] J. RYDBERG, *Acta Chem. Scand.* **14**, 157 (1960).

*Calculation procedure*

The following is a development of the equations upon which the computer calculations are based. Dividing both sides of equation (1) by $[L]$ gives for the $j$th point:

$$\bar{n}_j = \frac{\sum_{n=1}^{N} n\beta_n [L]_j^{n-1}}{1 + \sum_{n=1}^{N} \beta_n [L]_j^n} \tag{2}$$

where $N$ = number of complex species. For example, in the case of the trivalent lanthanides and glycolate anions where $ML^{2+}$, $ML_2^+$, $ML_3$ and $ML_4^-$ form, $N = 4$.

Now, let

$$R_j = \frac{\sum_{n=1}^{N} n\beta_n [L]_j^{n-1}}{1 + \sum_{n=1}^{N} \beta_n [L]_j^n} - \frac{\bar{n}_j}{[L]_j} \tag{3}$$

The least squares method for determining $\beta_n$ in equation (2) requires that

$$R = \sum_{j=1}^{k} R_j^2$$

be minimized with respect to $\beta_n$. This amounts to solving the following system of $N$ linear equations in the unknowns $\beta_1, \beta_2 \cdots \beta_N$:

$$\frac{\partial R}{\partial \beta_n} = 0;\ n = 1, 2, \cdots N$$

However, the term $1 + \sum_{n=1}^{N} \beta_n [L]_j^n$, in the denominator of equation (3) causes the expression $\partial R/\partial \beta_n$ to be too complicated to handle easily and the following treatment is used to achieve simplification. If the right side of equation (3) is altered by putting both terms over the common denominator $1 + \sum_{n=1}^{N} \beta_n [L]_j^n$, the result is

$$R_j = \frac{\sum_{n=1}^{N} n\beta_n [L]_j^n - \frac{\bar{n}_j}{[L]_j}\left[1 + \sum_{n=1}^{N} \beta_n [L]_j^n\right]}{1 + \sum_{n=1}^{N} \beta_n [L]_j^n} \tag{4}$$

The numerator of this equation (designated by $P_j$) may be simplified to

$$P_j = \frac{\bar{n}_j}{[L]_j} + \beta_1(\bar{n}_j - 1) + \beta_2(\bar{n}_j - 2)[L]_j + \cdots \beta_N(\bar{n}_j - N)[L]_j^{N-1} \tag{5}$$

Using $Q_j$ to represent the denominator in equation (4), we may write equation (4) as

$$R_j = \frac{P_j}{Q_j}$$

The problem then resolves itself into solving the system

$$\frac{\partial\left[\sum_{j=1}^{k}\left(\frac{P_j}{Q_j}\right)^2\right]}{\partial\beta_n} = 0;\ n = 1,2,\cdots N \tag{6}$$

To use equation (6), an arbitrary first guess, $\beta_1^1$, $\beta_2^1 \cdots \beta_N^1$, for the coefficients is made and $Q_j$ for these coefficients evaluated. The value obtained, designated as $Q_j^1$, is then used in equation (6) in place of $Q_j$, reducing the problem of solving equation (6) to the same as solving

$$\frac{\partial\left[\sum_{j=1}^{k}(P_j)^2\right]}{\partial\beta_n} = 0 \tag{7}$$

where the $j$th point is weighted by the inverse of $(Q_j^1)^2$ (for $j = 1, 2 \cdots k$). Since

$$Q_j = 1 + \sum_{n=1}^{N}\beta_n[L]_j^n = \frac{C_{M_j}}{[M]_j}$$

where $C_M$ = total concentration of metal ion and $[M]$ = concentration of uncomplexed metal ion, the procedure described has the byproduct effect of weighting the $j$th point by $[M]_j/C_{M_j}$ although such is not the direct intention.

When equation (7) is solved, a new set of approximations, $\beta_1^2$, $\beta_2^2 \cdots \beta_N^2$, is obtained. These may in turn be used to evaluate a new $Q_j^2$ and the process of solving equation (7) repeated for a new set $\beta_1^3$, $\beta_2^3 \cdots \beta_N^3$. This overall process is continued until the change from $\beta_n$ to $\beta_n^{i+1}$ is as small as desired. No mathematical proof of the convergence of this iteration is available, but for the lanthanide complexes where $N = 4$, it was observed that after four iterations of this procedure, the change from $\beta_n{}^i$ to $\beta_n^{i+1}$ did not affect the first three or four significant figures in $\beta_n{}^i$.

*Results*

The values of $\beta_n$ calculated by this least squares technique and by the graphical method are compared in Table 1 for several lanthanide systems. A more complete tabulation of stability constants computed by this technique is given in reference (8). $\bar{n}$ and $[L]$ data that vary according to the determinate errors of these quantities are used to calculate error limits for $K_1$, $K_2$ and $K_3$. For the systems of Table 1, these limits were approximately $\pm 5$ per cent for $K_1$, $\pm 10$ per cent for $K_2$ and $\pm 20$ per cent for $K_3$ which corresponds closely to the limits given for most graphical determinations. Although, the maximum experimentally observed ligand number in these systems is four, random computational errors often give rise to very large fluctuations in the values of $\beta_4$ making $K_4$ values rather unreliable. The accuracy of $K_4$ in these systems from graphical analysis is about one order of magnitude. As pointed out previously[11] and as should be obvious from the preceeding discussion, the least squares technique gives constants of the same reliability as the other calculation methods. Therefore, for any calculation method, it is of greatest importance to fashion the experiment so as to obtain very reliable $\bar{n}$ and $[L]$ data.

The data in Table 1 was calculated with an I.B.M. 650 computer; the time

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TABLE 1.—COMPARISONS OF $\beta_n$ VALUES CALCULATED GRAPHICALLY AND BY COMPUTER FROM THE SAME SETS OF $\bar{n}$ AND $[L]$ DATA

| Complex | $La^{+3}$-acetate[44a] | | $Gd^{+3}$-glycolate[14b] | | $Sm^{+3}$-lactate[8] | | $Sm^{+3}$-α-hydroxy-isobutyrate[8] | |
|---|---|---|---|---|---|---|---|---|
| Constant | Graphical | Computer | Graphical | Computer | Graphical | Computer | Graphical | Computer |
| 1 | 36 | 37 | 300 | 307 | 362 | 366 | 555 | 560 |
| 2 | 300 | 290 | $2{\cdot}7 \times 10^4$ | $2{\cdot}7 \times 10^4$ | $4{\cdot}2 \times 10^4$ | $3{\cdot}9 \times 10^4$ | $8{\cdot}4 \times 10^4$ | $7{\cdot}9 \times 10^4$ |
| 3 | 950 | 984 | $6{\cdot}2 \times 10^5$ | $6{\cdot}2 \times 10^5$ | $7{\cdot}5 \times 10^5$ | $8{\cdot}1 \times 10^5$ | $3{\cdot}4 \times 10^6$ | $3{\cdot}0 \times 10^6$ |
| 4 | 900 | 942 | $2{\cdot}6 \times 10^6$ | $2{\cdot}5 \times 10^6$ | — | — | — | — |

necessary to generate a set of constants from a series of $\bar{n}$ and $[L]$ values was approximately 20 min. With a faster computer such as the I.B.M. 709, this time would be shortened considerably.

Although RYDBERG *et al.* used the same basic equation as we do (i.e. equation 1), their algebraic treatment is different and the actual form to which the least squares technique is applied is

$$\sum_{n=1}^{N} (C_L - [L] - nC_M)\beta_n[L]^n = 0$$

This requires $C_L$, the total ligand concentration, and $C_M$, the total metal ion concentration, as well as $[L]$ for each titration point, whereas our system requires $\bar{n}$ and $[L]$. Both programs require previous calculation of the input data from the direct experimental data. The input data in Rydberg's programme must include the standard deviation in $[L]$ at each point. After the $\beta_n$ values are computed, they are used to compute the value that $[L]$ should have at each experimental point and these values are in turn used to calculate the standard deviation of the $\beta_n$ values. This is in contrast to our method of determining the error limits for the $\beta_n$'s which is more of a "brute force" technique. The weighting procedure used in our programme follows more from a simplification of the computational procedure whereas the other programme introduces a deliberate weighting technique. The net result is that the approach of RYDBERG *et al.* goes further than ours; however, it does this at the expense of greater complexity necessitating longer machine running time and more memory storage than the programme described in this article.

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# THE MASS SPECTRUM OF TRIMETHYLBOROXINE

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**Abstract**—Comparison of the mass spectra of isotopically normal and $^{10}B$-enriched trimethylboroxines makes possible the identification of the various fragments. The spectra furnish independent substantiation of the molecular weight and structure of $(CH_3)_3B_3O_3$—a ring with considerable aromatic character. The $^{10}B/^{11}B$ isotopic abundance ratio determined from the principal-peak region is 0·251. Theoretical considerations involving molecular vibrations are introduced to show that there are minimum isotopic effects on fragmentation, and consequently on the calculated abundance ratio, when bond rupture is produced by vibration of light atoms or groups against heavy boron-containing groups.

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THE natural isotopic abundance ratio of boron still is the subject of much controversy. Although handbooks[1,2] list a natural $^{10}B/^{11}B$ abundance ratio of 0·232 (obtained from the mass spectrum of $BF_3$),[3] investigators in the boron hydride field have found the value 0·25 to be more useful. To obtain further insight into this problem, we examined the mass spectra of some polyboron compounds that were not boron hydrides.

For boron hydrides, the "best" boron ratio is that which yields minimum residues in the calculation of monoisotopic spectra.[4,5] In the search for other boron compounds which could yield a more reliable value of the boron abundance ratio, several criteria were set:

(1) The compound should contain at least three boron atoms per molecule, with all other atoms having well-known isotopic distributions;
(2) preferably, the compound should not contain hydrogen atoms, to reduce the number of different fragments contributing to the same peak (e.g. $^{11}BCH$ and $^{10}BCH_2$);
(3) the compound should be easily prepared and purified and have a reasonable vapour pressure at room temperature.

The first criterion has not been fully appreciated in the past. In compounds containing a single boron atom, impurities can severely affect determination of isotope ratios. For instance, when the isotopic abundance is determined from a simple ratio, such as $^{10}BF_2$ to $^{11}BF_2$ fragments of boron trifluoride, impurities having peaks at $m/e$ 48 and/or 49 will obscure matters. The situation is not improved when a "stripping" process is used as for the hypothetical compound $BH_x$. There will be $x + 2$ peaks,

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ranging from $m/e$ 10 [$^{10}B$] to $m/e$ $(11 + x)$ [$^{11}BH_x$], from which we can determine $x + 1$ monoisotopic fragments [B, BH, . . . , $BH_x$] plus an abundance ratio. However, the picture is changed for multiple-boron fragments. For example, in diborane there are nine peaks between $m/e$ 20 [$^{10}B_2$] and 28 [$^{11}B_2H_6$], from which we can calculate the seven monoisotopic fragments and the abundance ratio and still have one peak as a checkpoint. For three-boron fragments, there remain two checkpoints.

Trimethylboroxine [$(CH_3)_3B_3O_3$] satisfactorily fulfills the first and the last of the above criteria. Although hydrogen atoms complicate the picture, we can nevertheless obtain a reliable monoisotopic fragmentation pattern through comparison of isotopically normal and $^{10}B$-enriched trimethylboroxine spectra.

## EXPERIMENTAL

### *Apparatus*

Standard high-vacuum techniques were employed in the preparation and handling of all materials. Mass spectra were obtained with a Consolidated Model 21-103C mass spectrometer, operating at an ionizing potential of 70 V. A Datatron 205 Computer was used for calculation of mass spectra as a function of the isotopic boron ratio.

### *Preparation*

Since a supply of isotopically labelled 1,2-dimethyldiboranes was available[6,7] it was deemed convenient to use these compounds as starting materials in the preparation of trimethylboroxine. 1,2-Dimethyldiborane was treated with excess water to form dihydroxymethylborane (methylboronic acid), which then was heated at 117–120°C in a sealed tube for several hours in the presence of anhydrous calcium chloride. Trimethylboroxine was distilled from the tube and purified.[8,9]

## RESULTS

### *Principal group, m/e* 107–113

The polyisotopic mass spectra for naturally occurring and $^{10}B$-enriched trimethylboroxines are given in Table 1. Comparison of the two spectra indicates that the principal peaks ($m/e$ 111 for $^{n}B$, and $m/e$ 108 for $^{10}B$) correspond to the species $C_2H_6B_3O_3$, representing the loss of one methyl group from the parent compound. The small peak in the $^{10}B$-enriched spectrum at $m/e$ 107 and the relative absence of any significant peak at $m/e$ 106 indicate that only one hydrogen atom is fragmented from the principal species. With this information it was possible to synthesize* a polyisotopic spectrum for various assumed $^{10}B/^{11}B$ ratios and then compare the calculated values of $m/e$ 109 and 110 with the observed values in the isotopically normal spectrum. In the synthesis of the polyisotopic spectrum, the following isotopic distributions for carbon, hydrogen, and oxygen were used:[11] $^{13}C/^{12}C = 0{\cdot}010811$, $D/H = 0{\cdot}00015$, $^{17}C/^{16}O = 0{\cdot}00040$, and $^{18}O/^{16}O = 0{\cdot}002005$.

Calculated polyisotopic spectra of $C_2H_6B_3O_3$ and $C_2H_5B_3O_3$ fragments for several values of the boron ratio in the vicinity of that expected for the $^{10}B$-enriched compound

* The synthesis of a polyisotopic spectrum from a monoisotopic spectrum is based on the assumption that the loss of a hydrogen from a methyl group is identical for $^{11}BCH_3$ and $^{10}BCH_3$. The validity of this assumption is supported by the identity of mass spectral patterns for the $^{10}BC_2H_x$ and $^{11}BC_2H_x$ fragments in trimethylborane.[10]

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TABLE 1.—POLYISOTOPIC SPECTRA OF ISOTOPICALLY NORMAL AND $^{10}B$-ENRICHED TRIMETHYLBOROXINES

| *m/e** | $(CH_3)_3{}^nB_3O_3$ | $(CH_3)_3{}^{10}B_3O_3$ | *m/e** | $(CH_3)_3{}^nB_3O_3$ | $(CH_3)_3{}^{10}B_3O_3$ |
|---|---|---|---|---|---|
| 130 | 0·04 | 0 | 71 | 0·93 | 0·02 |
| 129 | 0·04 | 0 | 70 | 0·68 | 0·06 |
| 128 | 0·10 | Trace | 69 | 30·79 | 0·31 |
| 127 | 0·49 | Trace | 68 | 21·67 | 2·99 |
| 126 | 12·62 | 0·03 | 67 | 5·64 | 26·80 |
| 125 | 9·80 | 0·25 | 66 | 0·74 | 5·47 |
| 124 | 2·79 | 2·26 | 65 | 0·15 | 0·44 |
| 123 | 0·48 | 12·46 | 64 | 0·08 | 0·07 |
| 122 | 0·15 | 0·51 | 63 | 0·07 | 0·09 |
| 121 | 0·08 | 0·13 | 62 | 0·04 | 0·04 |
| 120 | 0 | 0·13 | 61 | Trace | 0·05 |
| | | | 60* | 0·06 | Trace |
| 114 | 0·08 | Trace | 59* | 0·04 | Trace |
| 113 | 0·85 | Trace | 58 | 0·09 | Trace |
| 112 | 2·77 | 0·07 | 57 | 0·58 | 0·03 |
| 111 | 100 | 0·20 | 56 | 0·73 | 0·08 |
| 110 | 75·55 | 1·77 | 55·5 | 0·53 | 0 |
| 109 | 19·57 | 17·00 | 55 | 8·10 | 0·33 |
| 108 | 1·87 | 100 | 54·5 | 0·17 | 0·40 |
| 107 | 0·07 | 1·27 | 54 | 4·02 | 2·63 |
| 106 | 0 | Trace | 53·5 | 0 | 0·12 |
| | | | 53 | 2·63 | 4·25 |
| 103 | 0·09 | 0 | 52 | 1·08 | 1·42 |
| 102 | 0·09 | Trace | 51 | 0·35 | 0·74 |
| 98 | 0·45 | 0 | 50 | 0·11 | 0·28 |
| 97 | 0·89 | 0 | 49 | 0·05 | 0·10 |
| 96 | 0·91 | 0 | 48·5 | Trace | 0 |
| 95 | 0·46 | 0·43 | 48 | 0·06 | 0·02 |
| 94 | 0·16 | 0·62 | 47·5 | 0·06 | 0·01 |
| 93 | 0·05 | 0·39 | 47 | 0·07 | 0·03 |
| 92 | 0 | 0·06 | 46·5 | Trace | 0·03 |
| 91 | 0 | 0·03 | 46 | 0·03 | 0·07 |
| | | | 45 | 0·67 | 0·02 |
| | | | 44 | 0·46 | 0·10 |
| 86 | 0·05 | 0 | 43 | 13·05 | 0·36 |
| 85 | 0·80 | 0·02 | 42 | 8·43 | 5·12 |
| 84 | 1·72 | 0·10 | 41 | 11·60 | 3·74 |
| 83 | 1·27 | 0·74 | 40 | 6·57 | 6·71 |
| 82 | 0·57 | 1·15 | 39 | 3·63 | 2·25 |
| 81 | 0·56 | 0·44 | 38 | 1·30 | 2·40 |
| 80 | 0·27 | 0·21 | 37 | 1·73 | 0·81 |
| 79 | 0·29 | 0·30 | 36 | 0·61 | 1·10 |
| 78 | 0·14 | 0·11 | 35 | 0·12 | 0·12 |
| 77 | 0 | 0·17 | 34·5 | 0·14 | Trace |
| 76 | 0 | 0·04 | 34 | 0·11 | 0·06 |
| 75 | 0 | 0·02 | 33·5 | 0·12 | 0·02 |
| 74 | 0 | 0·02 | 33 | 0·07 | 0·08 |
| | | | 32·5 | 0·02 | 0·07 |
| 72 | 0·05 | 0 | 32 | 0·11 | 0·06 |

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TABLE 1 (*Contd.*)

| *m/e** | $(CH_3)_3{}^nB_3O_3$ | $(CH_3)_3{}^{10}B_3O_3$ | *m/e** | $(CH_3)_3{}^nB_3O_3$ | $(CH_3)_3{}^{10}B_3O_3$ |
|---|---|---|---|---|---|
| 31 | 0·11 | 0·05 | 17 | 0·02 | 0·02 |
| 30 | 0·08 | 0·03 | 16 | 0·27 | 0·13 |
| 29 | 2·94 | 0·55 | 15 | 11·79 | 6·68 |
| 28 | 2·00 | 1·79 | 14 | 2·90 | 1·63 |
| 27 | 2·11 | 0·51 | 13 | 2·22 | 0·31 |
| 26 | 3·93 | 1·07 | 12 | 1·48 | 1·39 |
| 25 | 1·86 | 2·39 | 11 | 4·90 | ~0·9†,‡ |
| 24 | 0·65 | 0·67 | 10 | ~1·3† | ~3·6† |
| 23 | 0·27 | 0·17 | | | |
| 22 | 0·09 | 0·19 | 2 | 0·30 | 0·13 |
| 21 | 0·02 | 0·09 | | | |
| 20 | 0 | 0·02 | Rel.** | | |
| 19 | 0 | 0 | sens. | 1·31 | 2·23 |
| 18 | 0·05 | 0·07 | | | |

* *m/e* 130–60 obtained on high-mass scale; *m/e* 59–11 obtained on intermediate scale; *m/e* 2 and 10 obtained on low-mass scale.
† Adjusted value from low-mass scale.
‡ Checks with intermediate-scale value obtained from another chart.
** Sensitivity of 100 peak (in scale divisions per micron) divided by sensitivity of *m/e* 43 peak of butane.

TABLE 2.—CALCULATED POLYISOTOPIC SPECTRA FOR VARIOUS BORON RATIOS ($^{10}$B-ENRICHED)

| $^{10}B/^{11}B$ | 19·5 | 20·0 | 20·5 | 21·0 | 21·5 | Observed |
|---|---|---|---|---|---|---|
| % $^{11}$B | 4·88 | 4·76 | 4·65 | 4·55 | 4·44 | |
| *m/e* | | | | | | |
| 110 | 1·77 | 1·72 | 1·68 | 1·64 | 1·60 | 1·77 |
| 109 | 17·82 | 17·44 | 17·07 | 16·73 | 16·39 | 17·00 |
| 108 | 100 | 100 | 100 | 100 | 100 | 100 |
| 107 | 1·27 | 1·27 | 1·27 | 1·27 | 1·27 | 1·27 |

are given in Table 2. It is apparent that the intensity value at *m/e* 109 is the most suitable for determination of the boron ratio; the relatively small intensity at *m/e* 110 eliminates this peak as a basis for comparison. The observed value at *m/e* 109 (17·0 units relative to 100 for *m/e* 108) indicates a $^{10}B/^{11}B$ ratio of 20·5, or a $^{11}B$ content of 4·65 (± 0·05) per cent.*

To determine the ratio for the isotopically normal compound, the relative peak intensities for *m/e* 109 and 110 were plotted as a function of the boron ratio (see Fig. 1). The basis for calculation is the ratio of (*m/e* 108)/(*m/e* 107) = 100/1·27 in the $^{10}B$-enriched spectrum. To show how the intensity values vary with the relative peak height of *m/e* 107, calculations based on the ratios 100/2·0 and 100/0·63 are included as dotted lines in Fig. 1. These latter two ratios are regarded as being far beyond the limits of error in measuring the relative peak height of *m/e* 107. The arrows in Fig. 1 for the observed relative intensities of *m/e* 109 and 110 (Table 1) correspond to a $^{10}B/^{11}B$ ratio of 0·2508 (± 0·0030), or a $^{10}B$ content of 20·05 (± 0·20) per cent.* The

* The estimated error allows for relative peak-height reproducibility (including instrument error and possible impurities) of ca. 1 per cent.

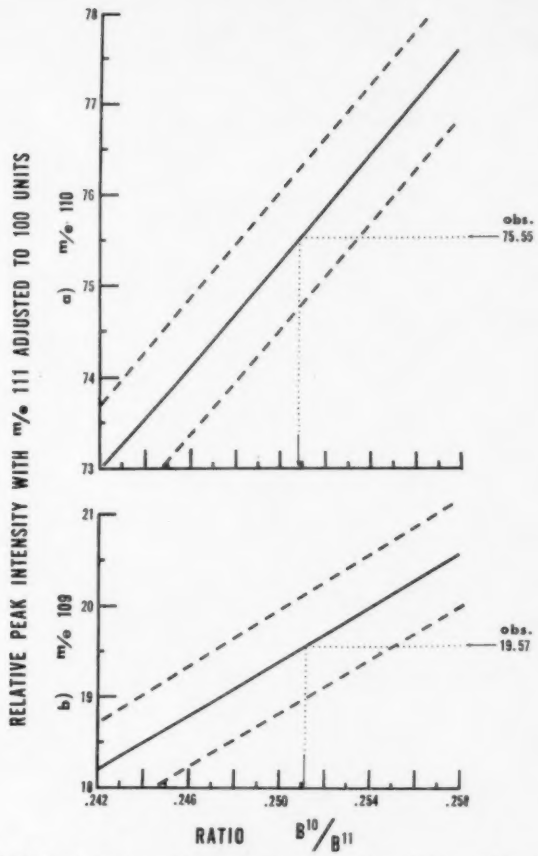


FIG. 1.—Calculated relative peak intensities of *m/e* 110 and 109 as a function of $^{10}B/^{11}B$ ratio.
——— based on ratio of 100/1·27 for *m/e* 108 to *m/e* 107 of $^{10}B$-enriched spectrum;
– – – – – extreme ratios of 100/0·63 and 100/2·0. Arrows indicate *observed* relative intensities.

good agreement between results obtained in Figs. 1(a) and (b) lends further support to this value.

*Parent group, m/e* 120–128

From Table 1, the identification of the fragmentation species can be ascertained by matching the relative intensities of comparable species in the two spectra. Obviously the groupings about *m/e* 126 in the $^{n}B$ spectrum, and *m/e* 123 in the $^{10}B$ spectrum, are attributable to the parent compound, $C_3H_9B_3O_3$. Using the same mathematical treatment as in the case of the principal species, one obtains boron ratios for the parent species in good agreement with those of the principal species, viz. 0·250 ± 0·003. The monoisotopic spectra of the four fragments of this group are listed in Table 3.

*Other mass groups*

The remaining monoisotopic fragment contributions (see Table 3) were obtained by standard techniques.[4,5,10] Some of these fragments involve rearrangements,

TABLE 3.—MONOISOTOPIC FRAGMENTATION PATTERN OF TRIMETHYLBOROXINE

| *m/e* | Fragment | Relative peak height |
|---|---|---|
| 128–120 | $C_3H_9B_3O_3$ | 12·45 |
| | $C_3H_8B_3O_3$ | 0·48 |
| | $C_3H_7B_3O_3$ | 0·10 |
| | $C_3H_6B_3O_3$ | 0·12 |
| 113–107 | $C_2H_6B_3O_2$ | 100 |
| | $C_2H_5B_3O_3$ | 1·27 |
| 98–93 | $CH_5B_3O_3$* | 0·40 |
| | $CH_4B_3O_3$* | 0·56 |
| | $CH_3B_3O_3$ | 0·40 |
| | $CH_2B_3O_3$ | 0·03 |
| 85–76 | $C_2H_8B_2O_2$* | 0·04 |
| | $C_2H_7B_2O_2$* ($CH_3B_2O_3$) | 0·60 |
| | $C_2H_6B_2O_2$ ($CH_2B_2O_3$) | 1·06 |
| | $C_2H_5B_2O_2$ ($CHB_2O_3$) | 0·43 |
| | $C_2H_4B_2O_2$ ($CB_2O_3$) | ~0·20 |
| | $C_2H_3B_2O_2$ | 0·29 |
| | $C_2H_2B_2O_2$ | 0·08 |
| | $C_2HB_2O_2$ | 0·17 |
| | $C_2B_2O_2$ | 0·03 |
| 72–64 | $CH_6B_2O_2$* | ≤0·03 |
| | $CH_5B_2O_2$* | 0·08 |
| | $CH_4B_2O_2$* | 0·15 |
| | $CH_3B_2O_2$ | 25 |
| | $CH_2B_2O_2$ | 5·2 |
| | $CHB_2O_2$ | 0·4 |
| | $CB_2O_2$ | 0·07 |
| 58–48 | $CH_3BO_2$ | ≤0·1 |
| | $CH_2BO_2$ | ≤0·1 |
| | $CHBO_2$ | 0 |
| | $CBO_2$ | ~1·6 |
| | $H_3B_2O_2$* | 0·3 |
| | $H_2B_2O_2$* | 0·4 |
| | $HB_2O_2$* | 4·0 |
| | $B_2O_2$ | ~0·5 |
| | $CH_3B_2O$ | 0·7 |
| | $CH_2B_2O$ | 0·25 |
| | $CHB_2O$ | ~0·1 |
| | $CB_2O$ | 0 |
| | $C_2H_2BO$† | 0·9 |
| | $C_2HBO$† | 0 |
| | $C_2BO$† | 0 |
| 45–35 | $H_2BO_2$* | 0·1? |
| | $HBO_2$* | ≤0·1 |
| | $BO_2$ $CH_4BO$* | 4·5 |
| | $CH_3BO$ | 3·0 |
| | $C_2H_6B$† $CH_2BO$ | 6·1–6·6‡ |
| | $C_2H_5B$† $CHBO$ | ~2·0 |
| | $C_2H_4B$† $CBO$ | ~1·5 |
| | $C_2H_3B$† | ~0·4 |
| | $C_2H_2B$† | 1·0 |
| | $C_2HB$† | 0·1 |
| | $C_2B$† | <0·1 |
| | $H_2B_2O$* | <0·5 |
| | $HB_2O$* | <0·5 |
| | $B_2O$ | 0 |
| 29–22 | $H_2BO$* $CH_6B$* | 1·6 |
| | $HBO$* $CH_5B$* | 0·8–0·4‡ |
| | $BO$ $CH_4B$* | ~0·9 |
| | $CH_3B$ | 2·2 |
| | $CH_2B$ | 0·6 |
| | $CHB$ | 0·15 |
| | $CB$ | 0·17 |
| 16–10 | $O_1$ | <0·1 |
| | $CH_3$ | 6·1–5·8‡ |
| | $CH_2$ | 1·4 |
| | $CH$ | 0·1 |
| | $C$ | <0·1 |
| | $BH_3$* | 0·1 |
| | $BH_2$* | 1·3 |
| | $BH$* | 0·6 |
| | $B$ | 3·0–~3·3‡ |
| 2 | $H_2$* | ~0·15 |
| | Doubly charged ions | |
| 55·5–53·5 | $C_2H_6B_3O_3$ | 0·53 |
| | $C_2H_5B_3O_3$ | 0·10 |

* Hydrogen-rearrangement.
† Skeletal rearrangement.
‡ Values from $^{11}B$ and $^{10}B$ spectra, respectively.

mostly of hydrogen atoms, but in a few cases (*m/e* 58–48 and 45–35) skeletal rearrangements of carbons are evident.

By careful comparison of the two polyisotopic spectra, most fragments could be identified and their relative contributions determined, even though their *m/e* values overlapped. However, in the *m/e* 45–35 and 29–22 regions we were unable to resolve some of these contributions.

Most groupings, for one reason or another, do not lend themselves to separate determinations of $^{10}B/^{11}B$ abundance ratios. But "stripping" of the low-mass region (*m/e* 16–10) is not possible with an assumed ratio of 0·25. Instead, an apparent abundance ratio of 0·28 is indicated.

## DISCUSSION

### *The fragmentation pattern*

Our mass spectra furnish independent substantiation of the molecular weight and structure of trimethylboroxine. The outstanding feature of the monoisotopic pattern (Table 3) is the scarcity of sizable peaks, with only three having relative values greater than 7 per cent. In two of these fragments, the $B_3O_3$ ring is intact. There seems to be no significant difference between the $(CH_3)_3{}^{11}B_3O_3$ and $(CH_3)_3{}^{10}B_3O_3$ patterns.

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A number of rearrangements are observed, at least one of them having a significant value ($HB_2O_2 = 4{\cdot}0$). Fragments involving skeletal rearrangements probably have peaks not greater than 1 per cent. (The larger peaks in the *m/e* 45–35 region are presumably due to $CH_xBO$ rather than $C_2H_xB$ fragments.) Only two doubly charged fragments make an appreciable contribution.

The mass spectra of trimethylboroxine and trimethylborane[10] have formal similarity in that the principal peaks in both represent loss of one methyl group. Both spectra have some rearrangement and half peaks and manifest different apparent abundance ratios for high- and low-mass fragments (see next section). Here the similarity ends.

Other familiar polyboron compounds, such as pentaborane-9[12,13] and hexaborane[14] have quite different fragmentation patterns, with a large number of significant peaks in the various mass groups.

Of special interest is the *dis*similarity of the spectrum of another boron ring-compound[15]—$[(CH_3)_2PBH_2]_3$. Broken-ring fragments of this unsaturated molecule have large spectral peaks. As a matter of fact, the principal fragment apparently is rearranged $(CH_3)_2B$.

The most striking parallelism occurs between trimethylboroxine and 1,3,5-trimethylbenzene (mesitylene).[16] This aromatic compound has only three peaks larger than 10 or 15 per cent, all three of them involving no ring fragmentation and, as in trimethylboroxine, the principal peak represents loss of one methyl group. On the other hand, the saturated hydrocarbon 1,3,5-trimethylcyclohexane[16] has many broken-ring fragments (including the principal fragment), like the previously mentioned phosphinoborine trimer.

These comparisons all confirm that trimethylboroxine has considerable aromatic

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[14] S. G. Gibbins and I. Shapiro, *J. Chem. Phys.* **30**, 1483 (1959).
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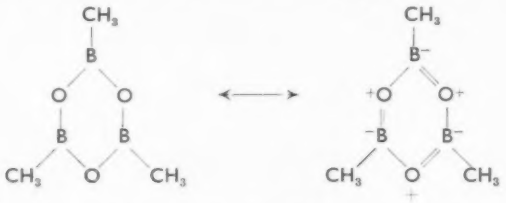
character, with resonance between structures of the type



*The $^{10}B/^{11}B$ ratios*

Different regions of the mass spectrum of this polyatomic compound yield distinct $^{10}B/^{11}B$ ratios: 0·251 for $C_2H_xB_3O_3$ (and $C_3H_xB_3O_3$), 0·28 for $BH_x$. Analogous findings have previously been reported for other boron compounds.[10,12,17–19]

This observation is not surprising in the light of our earlier contention[10,13,20] that these calculated ratios do not necessarily represent true abundance ratios, but include correction factors that compensate for differences in fragmentation of the various isotopic species. We have actually calculated such fragmentation correction factors for some simple compounds and correlated them with isotope masses and with vibrational frequency shifts.[21] For example, boron–boron bonds are split 8 per cent more easily in $^{10}B_2H_6$ than in $^{11}B_2H_6$. Similarly, judging from the apparent ratio of 0·28 in the low-mass region of $(CH_3)_3B_3O_3$, a single $^{10}B$ atom seems to split from the ring ca. 10 per cent more easily than a $^{11}B$ atom.

For certain types of fragmentation processes these isotope effects are expected to be quite small. The principal fragment of trimethylboroxine—$C_2H_6B_3O_3$—is produced by out-of-phase vibration of the relatively light methyl groups against a massive ring. Thus, the vibration should depend only to a small degree on whether the ring contains $^{11}B$ or $^{10}B$. This prediction is borne out by the small vibrational frequency shift[22] of 14 $cm^{-1}$, as compared to 29 $cm^{-1}$ for trimethylborane.[23] Hence, we expect little difference in the formation probabilities of $C_2H_6{}^{10}B_3O_3$ and $C_2H_6{}^{11}B_3O_3$. This means that a $^{10}B/^{11}B$ ratio obtained from that region of the spectrum should very nearly represent the true isotopic abundance.

This ratio, 0·25, is also obtained from the principal region of boron hydrides.[4,5,12–14,17,24,25] Here again, bond rupture is produced by variation of a light hydrogen atom against a relatively heavy boron atom, a vibration approximately independent of the boron mass. In contrast, B—C bond rupture in trimethylborane to produce its principal fragment, $BC_2H_6$, should exhibit considerable isotope effect; there we obtained[10] a $^{10}B/^{11}B$ ratio of 0·242.

In view of these isotope effects, one can expect to obtain true $^{10}B/^{11}B$ ratios directly from mass spectra only if they are determined from fragments that do not involve significant boron vibration in their formation.

*Acknowledgement*—The authors express their appreciation to Dr. J. C. PERRINE for his assistance with the computer program.

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# INFRA-RED SPECTROSCOPIC DETECTION OF BRIDGING CYANIDE GROUPS

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**Abstract**—Infra-red spectroscopic studies in the cyanide stretching region provide a means of distinguishing between terminal and bridging cyanide groups in various complex cyanides. The distinction lies in the observation that bridging cyanide groups exhibit a higher absorption frequency than do terminal cyanide groups.

The results are explained on the basis of a simple vibrational analysis of bridged versus non-bridged systems.

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DURING the last few years the technique of infra-red spectroscopy has been extensively applied to the study of co-ordination compounds.[1] In the present paper, infra-red studies in the cyanide stretching region for a series of complex cyanides are reported, and the results indicate that the cyanide stretching frequency for a bridging cyanide occurs at a higher value than if there were no bridging. In a recent paper, MITCHELL and WILLIAMS[2] reached a similar conclusion with regard to the cyanide stretching frequency for bridging thiocyanate groups.

## EXPERIMENTAL

*Preparation of compounds.* The preparations of $Ba_3[(NC)_5FeCNCo(CN)_5]\cdot 16H_2O$ and $[Ag_2Co(CN)_5\cdot 1{\cdot}5H_2O]_x$ have been previously described.[3] $K_4[Co(CN)_5S_2O_3]$ was prepared as described by RAY and DUTT.[4] $K_3[Co(CN)_6]$ was obtained following the method of BIGELOW.[5] $Ag_3[Co(CN)_6]$ precipitated upon mixing solutions of $K_3[Co(CN)_6]$ and $AgNO_3$; the white precipitate was filtered out, washed with water, and dried at 110°. $[Co(NH_2CH_2CH_2NH_2)_3][Co(CN)_5OH]$ was precipitated by adding acetone to a solution 0·1 M in $Co(NH_2CH_2CH_2NH_2)_3^{3+}$, 0·1 M in $Co(CN)_5OH^{3-}$ and 0·1 M in NaOH; the yellow solid was filtered out, washed with acetone, and dried in a vacuum desiccator over sulphuric acid. $[Na_2Co(CN)_5\cdot H_2O]_x$ was obtained by treating $[Ag_2Co(CN)_5\cdot 1{\cdot}5H_2O]_x$ with a solution containing the equivalent amount of sodium bromide, filtering out the silver bromide formed, and then evaporating the resulting solution in a vacuum desiccator over sulphuric acid. $[Na_2Co(CN)_5]_x$ was obtained by heating $[Na_2Co(CN)_5\cdot H_2O]_x$ at 100° under vacuum for 2 hr.

*Infra-red spectra.* The spectra were obtained with a Perkin-Elmer Model 13 spectrophotometer equipped with a $CaF_2$ prism, and calibrated with the rotational lines of carbon monoxide. Frequencies are believed accurate to two wavenumbers. Samples were studied both in Nujol mulls and in KBr pressed pellets in most cases.

## RESULTS AND DISCUSSION

Table 1 presents the results of our measurements, and also includes some pertinent data from the literature. It is seen from Table 1 that each spectrum of a Co(III) cyanide complex contains a strong absorption near 2130 $cm^{-1}$. Since the absorption at 2130 $cm^{-1}$ is the only one displayed by $K_3[Co(CN)_6]$, a compound in which cyanide

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TABLE 1.

| Compound | Mull* | Pellet* | Reference | Bonding |
|---|---|---|---|---|
| $K_3[Co(CN)_6]$ | 2130 *s* | 2131 *s*<br>2093 *w* | Present work | Co—CN |
| $K_4[Co(CN)_5S_2O_3]$ | | 2139 *s*<br>2126 *s*<br>2117 *s* | Present work | Co—CN |
| $[Co(en)_3][Co(CN)_5OH]$ | 2138 *sh*<br>2126 *s*<br>2114 *s* | 2138 *sh*<br>2127 *s*<br>2115 *s* | Present work | Co—CN |
| $[Na_2Co(CN)_5 \cdot H_2O]_x$† | 2202 *m*<br>2130 *s* | 2202 *m*<br>2135 *s* | Present work | Co—CN and Co—CN—Co |
| $[Ag_2Co(CN)_5 \cdot 1 \cdot 5H_2O]_x$† | 2170 *br*<br>2130 *s* | 2200 *m*<br>2131 *s* | Present work | Co—CN and Co—CN—Co |
| $Ag_3[Co(CN)_6]$ | 2187 *s*<br>2130 *m* | 2132 *s*<br>2095 *w* | Present work | Co—CN and Co—CN—Ag |
| $K_4[Fe(CN)_6]$ | 2047 *s* | | Present work | Fe(II)—CN |
| $Ba_3[FeCo(CN)_{11}] \cdot 16H_2O$ | 2130 *s*<br>2090 *m*<br>2055 *s* | 2131 *s*<br>2087 *m*<br>2076 *sh*<br>2050 *s*<br>2027 *m* | Present work | Co—CN, Fe(II)—CN and Fe(II)—CN—Co |
| AuCN | 2239 | | 7 | Au—CN—Au |
| $K[Au(CN)_2]$ | 2141‡ | | 8 | Au—CN |
| AgCN | 2164 | | 7 | Ag—CN—Ag |
| $K[Ag(CN)_2]$ | 2140‡ | | 8 | Ag—CN |
| CuCN | 2172 | | 7 | Cu—CN—Cu |
| $K[Cu(CN)_2]$ | 2125** | | 7 | Cu—CN |
| $Pd(CN)_2$ | 2220 | | 9 | Pd—CN—Pd |
| $K_2[Pd(CN)_4] \cdot H_2O$ | 2143 | | 9 | Pd—CN |
| $Ni(CN)_2$ | 2176 | | 9 | Ni—CN—Ni |
| $K_2[Ni(CN)_4] \cdot H_2O$ | 2128 | | 9 | Ni—CN |
| $Hg(CN)_2$ | 2193 | | 8 | Hg—CN—Hg |
| $K_2[Hg(CN)_4]$ | 2145** | | 6 | Hg—CN |

* Frequencies in wavenumbers, *s* = strong *m* = medium, *w* = weak, *sh* = shoulder, *br* = broad.
† Spectrum did not change on dehydration.
‡ Single crystal.
** Aqueous solution.

bridging certainly does not occur, we can reasonably assign this frequency to a cobalt (III) terminal cyanide. In the cases of $K_4[Co(CN)_5S_2O_3]$ and $[Co(NH_2CH_2CH_2NH_2)_3][Co(CN)_5OH]$, the effect of a decrease in symmetry of the complex is to be seen: three cyanide frequencies, grouped near the 2130 $cm^{-1}$ value, are observed.

Several compounds are found to exhibit, in addition to the terminal cyanide frequency at 2130 $cm^{-1}$, an absorption band at a significantly higher wavenumber. The polynuclear cobalt (III) pentacyanide $[Na_2Co(CN)_5 \cdot H_2O]_x$, for which chemical evidence[3] indicates that the polymerization is achieved through cyanide bridges between cobalt atoms, absorbs strongly at 2202 $cm^{-1}$. $Ag_3[Co(CN)_6]$ in Nujol mull

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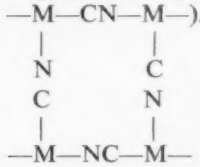
[7] R. A. PENNEMAN and L. H. JONES, *J. Chem. Phys.* **24**, 293 (1956).
[8] L. H JONES, *J. Chem. Phys.* **26**, 1578 (1957); **27**, 468, 665 (1957).
[9] M. F. A. EL-SAYED and R. K. SHELINE, *J. Inorg. Nucl. Chem.* **6**, 187 (1958).

absorbs strongly at 2187 $cm^{-1}$. $[Ag_2Co(CN)_5 \cdot 1 \cdot 5H_2O]_x$ exhibits a band at 2200 $cm^{-1}$ in the KBr pellet (2170 $cm^{-1}$, broad, in the mull). In each case, it seems appropriate to assign the higher frequency to a bridging cyanide with a structure either Co—CN—Co or Co—CN—Ag. Interesting differences between mull and pellet spectra point out some pitfalls in the pelletizing process. When $Ag_3[Co(CN)_6]$ is pressed in KBr the band at 2187 $cm^{-1}$ disappears, indicating an interchange which produces a $Co(CN)_6^{3-}$ ion in a KBr matrix. The $[Ag_2Co(CN)_5 \cdot 1 \cdot 5H_2O]_x$ sample was amorphous (no X-ray diffraction pattern was obtainable), and the broad 2170 $cm^{-1}$ band may be interpreted as indicating a large amount of disorder in bridging. However, the pellet spectrum is identical to that of the sodium salt, suggesting that the pelletizing has again produced ion interchange. Similar interchanges have been observed in other systems.*

$K_4[Fe(CN)_6]$ (no cyanide bridging) absorbs at 2047 $cm^{-1}$. We assign this frequency to Fe(II) terminal cyanide groups. The binuclear complex $Ba_3[(NC)_5FeCNCo(CN)_5] \cdot 16H_2O$ absorbs at 2055, 2090 and 2130 $cm^{-1}$. The first and last frequencies may be assigned to Fe(II) and Co(III) cyanide stretching vibrations. Due to the mode of preparation of the compound,[3] a bridging cyanide is expected to originate on the iron atom. Assignment of the 2090 $cm^{-1}$ absorption to the structure Fe—CN—Co is thus reasonable, and in agreement with our general thesis of increase in frequency on bridging. An alternate interpretation is possible in this case. The Raman spectrum of ferrocyanide ion in aqueous solution[6] contains frequencies of 2063 ($E_g$) and 2096 ($A_{1g}$) $cm^{-1}$ (the infra-red absorption occurs at 2041 $cm^{-1}$). Thus, the 2090 $cm^{-1}$ band in the binuclear iron-cobalt complex could be the ferrocyanide $A_{1g}$ made active by the decrease in symmetry of the ion. This coincidence of our assigned bridging frequencies and Raman frequencies[6] does not occur in any of our other examples. Furthermore, the infra-red spectra[10] of several heavy metal (Cu, Zn, Ni, Co, Mn, Cd, Fe) ferrocyanides show a single band at 2080 $\pm$ 15 $cm^{-1}$. In these compounds, as in prussian blue,[11] cyanide bridging to the cation is likely to occur, and the 2080 $cm^{-1}$ frequency when compared with that of $K_4[Fe(CN)_6]$ again demonstrates the frequency increase upon bridging.

In the lower part of Table 1 are collected data on various cyanides of copper and nickel group elements and mercury. The structures of the MCN salts[12] indicate that cyanide bridging occurs yielding di-co-ordinated copper group metal atoms (infinite chains of metal atoms connected by cyanide bridges M—CN—M—CN—M). The structures of $Ni(CN)_2$ and $Pd(CN)_2$ have not been reported, but it is likely[11] that cyanide bridging occurs yielding tetracoordinated metal atoms (sheets with the structure —M—CN—M—). The structure of $Hg(CN)_2$[14] indicates that each



* See the examples summarized in reference (1) p. 327.

[10] G. Emschwiller, *C. R. Acad. Sci., Paris* **238,** 1414 (1954).
[11] L. Pauling, *The Nature of the Chemical Bond*, p. 167. Cornell University Press, Ithaca (1960).
[12] (a) Structure of AgCN: C. D. West, *Z. Krist.* **90,** 555 (1935); (b) structure of AuCN: H. Zhdanov and E. Shugam, *Acta Phys. Chim. U.R.S.S.* **20,** 253 (1945).
[13] (a) A. F. Wells, *Structural Inorganic Chemistry*, p. 540. Oxford Univ. Press, London (1950).
(b) L. Pauling, *The Nature of the Chemical Bond*, p. 170. Cornell Univ. Press, Ithaca (1960).
[14] J. Hvoslef, *Acta Chem. Scand.* **12,** 1568 (1958).

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$Hg(CN)_2$ molecule interacts with two nitrogen atoms of neighbouring molecules. For each metal a datum is also presented for a complex ion with the same oxidation state and co-ordination number, but which does not involve cyanide bridging. In each case, the bridging cyanide frequency is higher than the terminal cyanide frequency.

Our criterion of comparing frequencies in different compounds with the same co-ordination number and oxidation number is in concert with the general discussion of cyanide frequencies by EL-SAYED and SHELINE,[9] and agrees with our observation that the ratio of co-ordination number to oxidation number determines the frequency within a narrow range. Thus, a survey of the literature on cyanide stretching frequencies in complex ions reveals the interesting fact that *all* transition metal cyanide complexes in which the co-ordination number is twice the oxidation number of the metal absorb infra-red radiation strongly at $2135 \pm 15\ cm^{-1}$. This observation covers some eighteen complexes ranging from chromium to mercury, and refers to non-bridging cyanide structures. Furthermore, it appears that increasing the co-ordination number to oxidation number ratio decreases the cyanide frequency, and vice versa.*

A simple vibrational analysis can perhaps explain the increase in cyanide frequency on bridging. As shown in the appendix, we may calculate approximate CN and MC force constants, as well as a MC—CN interaction force constant, from the data on, say, $K_3[Co(CN)_6]$. Two sets of possible force constants are obtained in the appendix. If we then simply use these force constants in the formulas for the frequencies in the bridging case, we obtain bridging frequencies of 2170 and 2150 $cm^{-1}$, for an increase over the terminal frequency of 20–40 $cm^{-1}$. A similar approach has been used before to compare free cyanide ion frequencies with those of complex cyanides,[15] and the P—O stretching frequency in triphenylphosphine oxide with the P—O stretching frequencies of various triphenylphosphine oxide complexes.[16]

If the bridging situation favours the triple bond between carbon and nitrogen (i.e. reduces the contribution of the double bonded resonance structure) the cyanide stretching force constant and thus the frequency would, of course, increase (the formulas in the appendix indicate a maximum of about 2280 $cm^{-1}$). However, the increase in the cyanide force constant is not required by the model: simply forming the bridge without changing any force constants will in itself raise the CN frequency. Physically this is because the presence of a second metal atom further constrains the motion of the cyanide group.

An alternate structure for the bridge involves bonding of the two metals through the carbon atom only, in analogy to the isoelectronic case of the metal carbonyls. While in some cases this alternate structure may be favourable (e.g. the $Ni_2(CN)_6^{4-}$ complex[17]), it seems that the present data and model favour the linear bridge, in agreement with structural data.[12]

## APPENDIX

We wish to set up a model of the vibrating systems involving terminal and bridging cyanide groups. We approximate these systems as M—CN and M—CN—M linear

* Some of these facts can be explained, at least qualitatively, in a manner similar to that used by EL-SAYED and SHELINE.[9] The explanation is based on the electroneutrality principle and the formation of $d$-$\pi$ bonds between metal and carbon.

[15] J. P. MATHIEU, *J. Chim. Phys.* **36**, 308 (1939).
[16] F. A. COTTON, R. D. BARNES and E. BANNISTER, *J. Chem. Soc.* 2199 (1960).
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structures, and assume that the metal atoms M have infinite mass to simplify the problem. A potential function for vibration along the M—CN—M axis is assumed:

$$2V = k_{CN}(x_N - x_C)^2 + k'(x_C)^2 + k'(x_N)^2 + 2k''(x_C)(x_N - x_C) - 2k''(x_N - x_C)(x_N)$$

where $x_i$ is the deviation of the $i$th atom from equilibrium. The metal–carbon and metal–nitrogen force constants $k'$ are assumed equal. This complete potential function includes an interaction constant $k''$ between the MC and CN bonds. In the non-bridged case, the third and fifth terms are absent. Solution of the two vibrational problems, with the usual assumption of harmonic motion, yields the following secular equations:

$$\text{for the terminal case} \quad \begin{vmatrix} k_{CN} + k' - 2k'' - \lambda m_C & k'' - k_{CN} \\ k'' - k_{CN} & k_{CN} - \lambda m_N \end{vmatrix} = 0$$

$$\text{for the bridging case} \quad \begin{vmatrix} k_{CN} + k' - 2k'' - \lambda m_C & 2k'' - k_{CN} \\ 2k'' - k_{CN} & k_{CN} + k' - 2k'' - \lambda m_N \end{vmatrix} = 0$$

where $\lambda$ is the wave number parameter, $\lambda = 4\pi^2 c^2 \nu^2$.

We wish to obtain values for the force constants, basing our calculations on $K_3[Co(CN)_6]$ where the terminal frequency is 2130 $cm^{-1}$. The metal carbon frequency is not of sensitive importance in this problem, and we take a typical frequency[18] of 450 $cm^{-1}$. The two frequencies allow determination of $k_{CN}$ and $k'$ if $k''$ is known. We assume that $k''$ is due to the contribution of a structure M=C=N[19] and that $k''$ has a positive sign, as is the case for structures of similar valence character,[20] e.g. $CO_2$. If we assume $k'' = 0{\cdot}1$ and $0{\cdot}5$ millidynes per angstrom, respectively, we obtain values of the other two force constants as in the following two possible sets:

$$k'' = 0{\cdot}1;\ k_{CN} = 16{\cdot}5;\ k' = 3{\cdot}25$$

$$k'' = 0{\cdot}5;\ k_{CN} = 17{\cdot}0;\ k' = 3{\cdot}14$$

For comparison, the force constant for CN in HCN (presumably a pure triple bonding situation) is 18·5 millidynes per angstrom. These two sets of force constants, when used in the secular determinant for the bridging case, yield CN frequencies of 2170 and 2150 $cm^{-1}$.

*Note added in proof*—We wish to thank Dr. L. H. JONES for pointing out that under certain circumstances our vibrational analysis can lead to a decrease in CN frequency on bridging. A somewhat more detailed analysis shows that an approximate condition for an increase is that the force constant $k'$ for the N—M bond must be at least four times the constant $k''$ for the CN—NM interaction. In this analysis the two ends of the bridge were not considered to have identical force constants, and the bridging attachment was considered as a perturbation. Since it seems likely that the condition on the force constants will be met, our previous conclusions are still valid.

[18] V. CAGLIOTI, G. SARTORI and M. SCROCCO, *J. Inorg. Nucl. Chem.* **8**, 87 (1958).
[19] L. PAULING, *Nature of the Chemical Bond*, p. 336. Cornell Univ. Press, Ithaca (1960).
[20] G. HERZBERG, *Infra-red and Raman Spectra*, p. 187. Van Nostrand (1945).

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# THE X-RAY POWDER DIFFRACTION PATTERN AND DENSITY OF SOLID PERCHLORYL FLUORIDE

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**Abstract**—The X-ray powder diffraction pattern and the density of solid $ClO_3F$ have been determined at liquid air temperatures. From the powder data it appears that crystalline $ClO_3F$ is tetragonal.

THE structure of the gaseous perchloryl fluoride molecule, $ClO_3F$, has been determined as a symmetric top from the infra-red spectrum.[1,2] The very small dipole moment, 0·023 debye units,[3] is consistent with this symmetrical structure. There are no previous reports on the structure of solid $ClO_3F$, but the entropy considerations of KOEHLER and GIAUQUE[4] suggest that in the crystal the fluorine and oxygen positions are ordered over only a limited range. The excess entropy is only a little less than $R$ ln 4, i.e. the molecules are apparently in rotational disorder.

The X-ray powder diffraction pattern at liquid air temperatures reported here gives further information on the crystal structure of perchloryl fluoride.

## EXPERIMENTAL

Perchloryl fluoride furnished by the Pennsalt Chemicals Corporation was passed through a 4 ft column of anhydrous magnesium perchlorate and condensed in a previously evacuated Vycor glass bulb at the end of a thin-walled capillary.

A North American Phillips 114·6 mm diameter powder camera was adapted for use with a liquid air delivery apparatus. Details of the experimental procedures are reported elsewhere.[5] In the samples studied, no lines attributable to carbon dioxide or ice crystals were found. Furthermore, the samples appeared to melt and freeze evenly, and the powder diffraction pattern was reproducible.

## RESULTS

The powder diffraction data for solid $ClO_3F$ presented in Table 1 as $10^4d^{-2}$ (obs.)—which is proportional to $\sin^2\theta$—were calculated from angles measured on a 10 hr exposure of Type K Kodak No-Screen X-ray Safety Film to nickel-filtered copper $K_\alpha$ diffraction with a 0·5 mm sample. The diffraction lines did not appear to have been broadened or blurred by any unusual effects; however, the background was dense and the contrast was poor so the intensities were only roughly estimated.

The density of solid perchloryl fluoride was measured by marking the height in a Pyrex tube of the solid frozen in liquid air, then weighing the tube before and after the perchloryl fluoride was allowed to escape. Densities of 2·208 and 2·175 g/cm³ were measured by comparison with the mass of mercury filling the tube to the same mark. Negative errors of 2 per cent or less may result from the presence of cracks in the solid. Thus, the density at −190°C is 2·19 ± 0·02 g/cm³.

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[2] R. P. MADDEN and W. S. BENEDICT, *J. Chem. Phys.* **25**, 594 (1956).
[3] A. A. MARYOTT and S. J. KRYDER, *J. Chem. Phys.* **27**, 1221 (1957).
[4] J. K. KOEHLER and W. F. GIAUQUE, *J. Amer. Chem. Soc.* **80**, 2659 (1958).
[5] R. L. TALLMAN, Ph.D. Thesis, University of Wisconsin (1960).

TABLE 1.—OBSERVED POWDER DIFFRACTION LINES FOR $ClO_3F$

| Line No. | $10^4 d^{-2}$ (obs.) | Relative intensity (very rough) | *hkl* indices | $10^4 d^{-2}$ (calc.) |
|---|---|---|---|---|
| 1 | 0689 | 100 | 200 | 0682 |
| 2 | 1027 | 10 | 201 | 1037 |
| 3 | 1719 | 12 | 221 | 1718 |
| 4 | 2037 | 0·1 | 311 | 2059 |
| 5 | 2539 | 1 | 321 | 2570 |
| 6 | 2766 | 2 | 222 | 2783 |
| 7 | 3266 | 0·2 | 411 | 3251 |
| 8 | 3756 | 0·1 | 421 | 3763 |
| 9 | 4060 | 0·1 | 213 | 4047 |
| 10 | 4169 | 0·5 | 402 | 4146 |
| 11 | 4287 | 0·1 | 500; 430<br>412 | 4260<br>4316 |
| 12 | 4726 | 0·1 | 303 | 4729 |
| 13 | 4840 | 0·9 | 422 | 4828 |
| 14 | 5389 | 0·1 | 323 | 5411 |
| 15 | 6311 | 0·1 | 610 | 6305 |
| 16 | 6815 | 0·2 | 620 | 6816 |
| 17 | 7239 | 0·1 | 304 | 7214 |
| 18 | 8112 | 0·1 | 429 | 8088 |
| 19 | 8777 | 0·1 | 334 | 8747 |
| 20 | 9330 | 0·1 | 604 | 9329 |

From the ratios of the observed spacings crystalline perchloryl fluoride appears to be tetragonal. An indexing of all the lines gives a unit cell with lattice parameters $a = b = 7{\cdot}66$ Å, $c = 5{\cdot}31$ Å. The calculated density for four $ClO_3F$ species per unit cell is 2·18 g/cm³ in agreement with the observed density value given above. The calculated $d^{-2}$ spacings and their corresponding indices are also given in Table 1.

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# EVIDENCE FOR TWO NEW CRYSTALLINE FORMS OF SODIUM PEROXIDE

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**Abstract**—A diffractometer equipped with a special furnace was used to record the powder diffraction pattern of $Na_2O_2$ over the range 25–550°C. A new phase, $Na_2O_2$-II, is stable at high temperatures. The transition temperature was found from diffractometer and separate thermal analysis measurements to be 512 ± 1°C.

The thermal expansion coefficient of $Na_2O_2$-I, from diffractometer data, was found to be essentially isotropic and linear within the limit of error, and equal to $(2{\cdot}84 \pm 0{\cdot}4) \times 10^{-5}$ °C$^{-1}$ (15–460°C).

Samples prepared by pouring molten sodium peroxide into liquid air gave a powder diffraction pattern at room temperature which is tentatively identified as that of a third polymorph, $Na_2O_2$-*Q*.

TODD[1] has measured the low temperature heat capacity of sodium peroxide, from 52°K to room temperature, and has found no maxima or discontinuities in the heat capacity curves. In work reported here, the X-ray powder diffraction pattern as measured by a Geiger-counter diffractometer did not change significantly, except as a result of thermal expansion, over the temperature range 15–500°C. At about 510°C the pattern changed entirely, and a new set of peaks was obtained which must be characteristic of a new structure and a new phase.

RODE and GOL'DER[2] attributed to melting an endothermic effect at 510°C in the differential thermal analysis heating curve of sodium peroxide. FÖPPL[3] found a thermal anomaly at 485°C in both heating and cooling curves. CHANDRASEKHARAIAH *et al.*[4] measured the heat content of $Na_2O_2$ to within about 80° of the melting point, using a drop-type calorimeter. A discontinuity (or point of inflexion) in the heat content curve was bracketed by measurements at 497 and 521°C. The heat of the transition was calculated to be 1280 cal mole$^{-1}$.

## EXPERIMENTAL

The furnace and sample holder were used with a General Electric XRD-3 diffractometer and are described elsewhere.[5] The sample, a $\frac{3}{4}$ in. pressed disk of sodium peroxide powder, was mounted vertically between magnesium oxide crystal plates in a slot in a $\frac{13}{16}$ in. stainless steel bar. Use of the horizontal focal spot (point focus) allowed positioning of the magnesium oxide front pieces over all but a $\frac{1}{4}$ in. horizontal strip of sample. This helped to prevent distortion of the surface of the sample. In addition, fine magnesium oxide powder was mixed with the sodium peroxide, about 1:1, for some of the runs; the surfaces of these samples remained very flat and smooth. The sodium peroxide was protected by one layer of ordinary household aluminium foil (0·0007 in. thick) tied down to the bar with wire. A slot in the end of the bar positioned the sample on a pedestal in the furnace. The furnace

[1] S. S. TODD, *J. Amer. Chem. Soc.* **75**, 1229 (1953).
[2] T. V. RODE and G. A. GOL'DER, *Izvest. Akad. Nauk SSSR, Otd. Khim. Nauk* 299 (1956); Translation 96HIOR of the Associated Technical Services.
[3] H. FÖPPL, *Z. Anorg. Chem.* **291**, 12 (1957).
[4] M. S. CHANDRASEKHARAIAH, R. T. GRIMLEY and J. L. MARGRAVE, *J. Phys. Chem.* **63**, 1505 (1959).
[5] R. L. TALLMAN, Thesis, University of Wisconsin (1960).

windows were of 0·00035 in. nickel foil, and provided the standard filter thickness for copper radiation.

Magnesium perchlorate-dried oxygen was condensed in a liquid air-cooled cold trap and allowed to flow through the furnace under slight pressure by bubbling the vented gas through vacuum pump oil. The sample was thus satisfactorily protected from contamination until the temperature was measured (after the diffraction measurements) by pushing the thermocouple (in an O-ring seal) through the aluminium foil and into the surface of the sample. The thermocouple was calibrated by measuring the temperature, 573°C, of the $\alpha$-$\beta$ transition of some colourless natural quartz.[6] This, as well as other calibrations, showed that the temperature as measured by the thermocouple was, at most, about 10°C lower than that of the surface of the sample.

Operations were performed in a dry-box or while the sodium peroxide was otherwise protected from water and carbon dioxide. Fresh Baker and Adamson sodium peroxide was ground as fine as possible by mortar and pestle and pressed under 900 atm in an evacuated die. Debye-Scherrer patterns of the powdered material and room temperature diffractometer patterns of the pressed samples showed only sodium monoxide impurity. This would be expected to oxidize to sodium peroxide in air and the sodium monoxide diffractometer peaks were observed to disappear when the sample was heated.

Adjustment of the position of the sample in the beam was possible at any time. The whole furnace was translated normal to the sample surface by $\frac{1}{4}$-28 Allen head cap screws. The line-up slit beam (narrow and more parallel) and the 0·02°$\theta$ detector slit at 0°2$\theta$ were used in this adjustment. It was assumed that moving the sample into the beam until the recorded intensity was reduced by a factor of two placed the sample in the centre of the beam. This alignment was suggested by Dr. H. W. PICKETT of the General Electric X-ray Department, Milwaukee, Wisconsin, and is essentially that described TOURNARIE,[8] which employed a "shielding wedge", and applied by SMAKULA and KALNAJS.[9] TOURNARIE found his adjustment to be reproducible to 2–3$\mu$, which is about 0·0001 in., the same as was found for the apparatus described here.

Measurements of four quartz diffraction angles between 20° and 40°2$\theta$, after correction for adsorption, flat-sample, and vertical divergence errors, agreed to within less than 0·03°2$\theta$ with angles calculated from the quartz lattice constants given by KEITH:[7] $a = 4{\cdot}91304$ Å, $c = 5{\cdot}40463$ Å. The errors introduced by the apparatus into the corrected angles for $Na_2O_2$-II are judged to have been no greater than $\pm$0·04°2$\theta$ in absolute value. Variations in the beam and detector slits and other misalignments in the machine thus had relatively minor effects on the results reported here.

## DIFFRACTION DATA

The information in Table 1 was taken from peaks recorded at 0·2°2$\theta$/min. and 24 in/hr chart speed. The recording time constant was the most rapid available, 3 sec. The important part of the scale, covering about 8 in., was logarithmic, from 25 to 10,000 counts/sec and the relative intensities were estimated from peak maxima corrected for background. The centres of gravity of the best-measured peaks were estimated by eye, averaging the angles of half-maximum intensity. Corrections were made for flat-sample,[10] absorption,[10] vertical divergence,[10] recorder lag (0·01°2$\theta$) and pen misalignment (0·01°2$\theta$) errors and estimates of the possible errors in the 2$\theta$ values were used in calculating the errors given for the $d^{-2}$ values. The $d^{-2}$ values from resolved $\alpha_1$ and $\alpha_2$ peaks were averaged. The wavelengths 1·54051, 1·54433 and 1·54178 Å were used for Cu$K\alpha_1$, Cu$K\alpha_2$ and the weighted average, respectively.

For well-behaved samples, including quartz, magnesium oxide and fresh sodium peroxide, the centres of gravity were reproducible with time and from sample to sample to within 0·01°2$\theta$. The relative intensities, and centres of gravity for $Na_2O_2$

[6] M. L. KEITH and O. F. TUTTLE, *Amer. J. Sci.* Bowen Volume, 203 (1952).
[7] H. D. KEITH, *Proc. Phys. Soc. Lond.* **63B**, 1034 (1950).
[8] M. TOURNARIE, *J. Phys. Radium* **15**, 11A (1954).
[9] A. SMAKULA and J. KALNAJS, *Phys. Rev.* **99**, 1737 (1955).
[10] H. P. KLUG and L. E. ALEXANDER, *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, p. 235–259. J. Wiley, New York (1954).

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patterns varied from sample to sample, varied with time for one sample, and varied with repeated transitions to and from the low temperature phase. The different peaks apparently varied independently. The average deviations of the centres of gravity for $Na_2O_2$-II were about 0·03°2$\theta$.

Average deviations in relative intensities ranged from 15 to 50 per cent for the best-measured peaks; a few peaks at high angles were recorded only once. These

TABLE 1.—$Na_2O_2$-II DIFFRACTOMETER PEAKS (550°C)

| Relative intensity | $10^4 d^{-2}$ ($A^{-2}$) | Relative intensity | $10^4 d^{-2}$ ($A^{-2}$) |
|---|---|---|---|
| 100 | 0815 ± 4 | *w* | 5635 ± 14 |
| 35 | 1078 ± 4 | *w* | 6191 ± 20 |
| 15 | 1353 ± 4 | *w* | 6304 ± 20 |
| 10 | 1416 ± 4 | *w* | 6504 ± 20 |
| 80 | 1961 ± 10 | *w* | 6749 ± 20 |
| 75 | 2166 ± 6 | *w* | 6828 ± 10 |
| *w* | 2368 ± 15 | *w* | 7248 ± 10 |
| *w* | 2460 ± 15 | *w* | 7310 ± 10 |
| *w* | 2727 ± 15 | *w* | 7853 ± 20 |
| 10 | 2999 ± 6 | *w* | 7970 ± 20 |
| 35 | 3051 ± 6 | *w* | 8308 ± 20 |
| *w* | 3176 ± 12 | *w* | 9041 ± 20 |
| *w* | 3245 ± 6 | *w* | 9174 ± 20 |
| *w* | 3558 ± 6 | *w* | 9500 ± 20 |
| *w* | 4371 ± 7 | *w* | 10099 ± 10 |
| *w* | 4570 ± 7 | *w* | 10577 ± 10 |
| *w* | 4630 ± 7 | *w* | 10905 ± 15 |
| *w* | 5172 ± 7 | *w* | 11123 ± 10 |
| *w* | 5410 ± 20 | *w* | 11592 ± 20 |
| *w* | 5497 ± 14 | *w* | 11688 ± 20 |
| | | *w* | 12167 ± 20 |

variations in the peak shapes, sizes, and angles probably resulted from the development of oriented crystals distributed in a non-random fashion across the surface of the samples. Reduction of the contamination by water-vapour and also the addition of magnesium oxide powder were found to reduce the extent of these variations.

## THERMAL EXPANSION COEFFICIENT OF $Na_2O_2$-I

Diffractometer measurements[5] of the diffraction angles of sodium peroxide at about 15, 350 and 450°C were used to calculate the linear expansion coefficients, $\alpha_{hkl}$, of the *d*-spacings of sodium peroxide. Sodium peroxide is hexagonal[3,11] at these temperatures and the powder diffraction pattern has been indexed.[5,12] It can be shown[5] that a plot of $\alpha_{hkl}$ vs. $d^2l^2$ should lie on a straight line of slope $(\alpha_c - \alpha_a)/c^2$ with intercept $\alpha_a$. The plots of $\alpha_{hkl}$ values calculated from seventeen diffraction peaks between 35 and 87°2$\theta$ are so scattered that, within the limits of error of the measurements, $\alpha_a = \alpha_c = (2{\cdot}84 \pm 0{\cdot}4) \times 10^{-5}$ °C$^{-1}$ for the temperature range investigated.

[11] R. L. TALLMAN, J. L. MARGRAVE and S. W. BAILEY, *J. Amer. Chem. Soc.* **79**, 2979 (1957).
[12] *X-ray Powder Data File*, American Society for Testing Materials (Card No. 9–75).

## OBSERVATIONS OF THE TRANSITION

The thermocouple used for temperature measurement was standardized with quartz by recording continuously the intensity at 66·50°2$\theta$ (at the low-angle base of the 212 peak of the low temperature phase) while the temperature was varied. The $\alpha$-$\beta$ transition brings an increased $d$-spacing and the peak angle is decreased by about 0·25°2$\theta$ to about 66·50°2$\theta$. The rate of increase in recorded intensity was observed to depend on the rate of increase in temperature because of thermal gradients across the sample and also, perhaps, because the transition was continuous.

The intensity changes recorded at the 111 peak angle (at about 35·5°$\theta$, for the low temperature phase, $Na_2O_2$-I) were definite but less reproducible in magnitude and in temperature than were those recorded for the quartz. The quartz transition was observed six times; the sodium peroxide transition was observed twenty times altogether using diffractometer intensity changes in five different samples, at thermocouple "temperatures" from 490 to 520°C.

When the $Na_2O_2$ sample has been exposed to water-vapour, the high temperature phase appears darker, and the boundary is followed most readily. Transitions to the high temperature phase were observed visually in five samples mounted in the diffractometer furnace. Temperatures from 490 to 504°C were measured as the phase boundary passed the thermocouple.

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## THERMAL ANALYSIS

Heating curves were obtained by driving an auto-transformer powering a furnace coil with a constant speed motor while measuring the potential of an 18-gauge chromel–alumel thermocouple immersed in about 2 g of sodium peroxide contained in an alumina crucible. The heating rate of about 1°C/min was sufficiently rapid that the thermocouple parted only in the region of the melting point of sodium peroxide (675°C, according to BUNZEL and KOHLMEYER[13]). Thermocouple potentials (with an ice bath cold junction) of 21·15 and 21·17 mV were measured while the temperature remained constant for at least 3 min. The transition temperature thus measured, under 1 atm of oxygen, is 512 $\pm$ 1°C.

## QUENCHED SODIUM PEROXIDE

A material, $Na_2O_2$-$Q$, prepared by pouring molten sodium peroxide into liquid air, gives an X-ray powder pattern[5] (Table 2) entirely different from that of $Na_2O_2$-I or $Na_2O_2$-II. This may be a polymorph stable above some temperature between 596°C, the highest temperature investigated calorimetrically,[4] and 675°C, the melting point,[13] or a new low temperature form. A standard 114·6 mm diameter North American Phillips camera was used with nickel-filtered copper $K\alpha$ radiation to obtain the data for Table 2.

## DISCUSSION

The use of various charts for cubic, hexagonal, tetragonal and rhombohedral indexing,[14] the procedure of VAND and ZSOLDOS[15,16] and the method of ITO[14]

[13] E. G. BUNZEL and E. J. KOHLMEYER, *Z. Anorg. Chem.* **254**, 1 (1947).
[14] As discussed in L. V. AZAROFF and M. J. BUERGER, *The Powder Method in X-ray Crystallography*. McGraw-Hill, NewYork (1958).
[15] V. VAND, *Acta Cryst.* **1**, 290 (1948).
[16] L. ZSOLDOS, *Acta Cryst.* **11**, 835 (1958).

TABLE 2.—X-RAY POWDER DIFFRACTION PATTERN OF $Na_2O_2$-$Q$ (TAKEN AT ROOM TEMPERATURE)

| Relative intensity | $10^4 d^{-2}$ ($A^{-2}$) | Relative intensity | $10^4 d^{-2}$ ($A^{-2}$) | Relative intensity | $10^4 d^{-2}$ ($A^{-2}$) |
|---|---|---|---|---|---|
| 0·1 | 453 | 1 | 4217 | 5 | 8943 |
| 90 | 697 | 7 | 4352 | 1 | 9132 |
| 2 | 845 | 12 | 4580 | 4 | 9308 |
| 45 | 1048 | 4 | 4803 | 4 | 9368 |
| 2 | 1077 | 1 | 5127 | 2 | 10332 |
| 45 | 1201 | 1 | 5317 | 2 | 10788 |
| 1 | 1404 | 5 | 5552 | 5 | 10974 |
| 10 | 1684 | 1 | 5690 | 1 | 11500 |
| 2 | 2021 | 11 | 5886 | 1 | 11738 |
| 100 | 2277 | 1 | 6057 | 4 | 12424 |
| 1 | 2519 | 5 | 6261 | $1\alpha_1$ | 14098 |
| 50 | 2776 | 1 | 6750 | $1\alpha_1$ | 14333 |
| 1 | 2931 | 2 | 7230 | $1\alpha_1$ | 14582 |
| 20 | 3101 | 5 | 7448 | 5B | 15163 |
| 12 | 3228 | 5 | 7845 | $1\alpha_1$ | 15471 |
| 4 | 3796 | 1 | 8176 | $1\alpha_1$ | 16536 |
| 1 | 4089 | 5 | 8499 | | |

failed to yield any satisfactory indexing of the $Na_2O_2$-II pattern. No extensive effort has been made to index the $Na_2O_2$-$Q$ pattern, but it is not cubic.

It is unfortunate that the structures of these phases are not readily obtainable. They should be useful in explaining some of the unusual phenomena associated with sodium peroxide. Molten sodium peroxide is black while crystalline $Na_2O_2$ is apparently non-stoicheometric, paramagnetic and yellow (yet a single-phase material),[5] as is sodium superoxide, $NaO_2$.

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# AMMONIUM, POTASSIUM, RUBIDIUM AND CESIUM HEXAVANADATES

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**Abstract**—The following anhydrous alkali hexavanadates have been prepared and shown to be isostructural: $K_2V_6O_{16}$, $(NH_4)_2V_6O_{16}$, $Rb_2V_6O_{16}$ and $Cs_2V_6O_{16}$. They are monoclinic and contain six vanadium atoms per unit cell. The crystal lattice undergoes a linear expansion in the *a* and *e* dimensions as the ionic radius of the cation increases. The hexavanadates of lithium and sodium could not be prepared.

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IN the phase diagram of the system $NH_3$–$V_2O_5$–$H_2O$,[1] the only stable solid phase in the polyvanadate region was shown to be anhydrous ammonium hexavanadate, $(NH_4)_2V_6O_{16}$. This compound has been previously mentioned in the literature.[2,3,4] An analogous potassium compound, $K_2V_6O_{16}$, has also been described.[2,5,6] BLOCK[7] determined the crystal structure of potassium hexavanadate. The crystals were orange, monoclinic, with space group $P2_1/m$ and one formula weight per unit cell. The structure contains vanadium atoms having five- and six-fold co-ordination of oxygen atoms. The vanadium atoms form linked zigzag chains that combine to form sheets. A series of experiments have been carried out by the author to see if other anhydrous alkali hexavanadates exist and to investigate structural relationships among them.

## EXPERIMENTAL

The general procedure followed in the preparation of these compounds involved the digestion at elevated temperature and constant volume of acidified metavanadate solutions. The starting solutions of approximately one molar alkali metavanadate were prepared by dissolving the desired alkali, as the hydroxide or carbonate, and pure $V_2O_5$ in water at a 1:1 mole ratio of alkali to vanadium. A small amount of $H_2O_2$ was added to insure complete oxidation of the vanadium to the pentavalent state. The resulting colourless to very pale yellow solutions were filtered to remove any undissolved solids.

The precipitation reactions were carried out in three-neck flasks equipped for stirring and refluxing to maintain constant volume at a controlled temperature of 85°C. The metavanadate solutions were preheated to 85°C before the acid addition. A quantity of acid approximately equivalent to that required by the following reaction was added:

$$6MVO_3 + 4H^+ = M_2V_6O_{16} + 4M^+ + 2H_2O$$

Sulphuric, hydrochloric or perchloric acid was used in various tests. After the acid addition the colourless metavanadate solutions turned deep red and orange crystals slowly formed. The resulting slurries were stirred for 24 hr at 85°C, then the precipitates were filtered, washed thoroughly with water and dried at 110°C to remove occluded water.

[1] A. D. KELMERS, *J. Inorg. Nucl. Chem.* In press.
[2] J. W. MELLOR, *Inorganic and Theoretical Chemistry*, pp. 757–766. Longmans, Green, London (1928).
[3] M. LACHARTRE, *Bull. Soc. Chim.* **35**, 321 (1924).
[4] J. B. MARTINEZ and C. GUILLEM, *Anales Real. Soc. Espan. Fis. y Quim.* **53** B 735 (1957).
[5] K. F. JAHR and G. JANDER, *Z. Anorg. Chem.* **220**, 201 (1934).
[6] J. BELTRAN and C. GUILLEM, *Anales Real. Soc. Espan. Fis. y Quim.* **55** B 149 (1959).
[7] S. BLOCK, Thesis, Johns Hopkins University (1955).

The chemical analyses of the anhydrous hexavanadates obtained are shown in Table 1. The vanadium was analysed as previously described.[1] The ammonia was determined by Kjeldahl techniques. Potassium was determined by the internal standard flame photometer method and rubidium and cesium by X-ray fluorescence techniques.

TABLE 1.—CHEMICAL ANALYSES

| | Experiment | $K_2O$ (%) | $V_2O_5$ (%) | Mole ratio K/V |
|---|---|---|---|---|
| Potassium | 1 | 14·3 | 85·2 | 0·33 |
| | 2 | 14·5 | 85·0 | 0·33 |
| | 3 | 14·2 | 84·1 | 0·33 |
| | 4 | 14·2 | 84·5 | 0·33 |
| | Average | 14·3 | 84·7 | 0·33 |
| | Calc. for $K_2V_6O_{16}$ | 14·7 | 85·3 | 0·33 |
| | Experiment | $(NH_4)_2O$ (%) | $V_2O_5$ (%) | Mole ratio $NH_4$/V |
| Ammonium | 1 | 8·3 | 89·9 | 0·32 |
| | 2 | 7·8 | 90·5 | 0·30 |
| | 3 | 8·4 | 91·3 | 0·32 |
| | Average | 8·2 | 90·6 | 0·32 |
| | Calc. for $(NH_4)_2V_6O_{16}$ | 8·7 | 91·3 | 0·33 |
| | Experiment | $Rb_2O$ (%) | $V_2O_5$ (%) | Mole ratio Rb/V |
| Rubidium | 1 | 25·6 | 74·2 | 0·34 |
| | 2 | 22·2 | 74·5 | 0·29 |
| | 3 | 21·2 | 74·0 | 0·28 |
| | 4 | 26·9 | 73·2 | 0·36 |
| | Average | 24·0 | 74·0 | 0·32 |
| | Calc. for $Rb_2V_6O_{16}$ | 25·5 | 74·5 | 0·33 |
| | Experiment | $Cs_2O$ (%) | $V_2O_5$ (%) | Mole ratio Cs/V |
| Cesium | 1 | 34·4 | 65·6 | 0·34 |
| | Calc. for $Cs_2V_6O_{16}$ | 34·0 | 66·0 | 0·33 |

The X-ray powder diffraction patterns were obtained by a composite technique. The stronger lines were located accurately with a Phillips wide range goniometer using filtered iron $K_\alpha$ radiation. However, due to fluorescence the weaker lines could not be observed. They were measured with Debye-Scherrer cameras using filtered chromium $K_\alpha$ radiation. The patterns obtained in this manner contained 50–70 lines. The major lines, indexed as described below, are shown in Table 2.

## DISCUSSION

Anhydrous hexavanadates of potassium, ammonium, rubidium and cesium were prepared. They were all orange, crystalline solids and the analyses were in good agreement with the calculated composition. Corresponding compounds of sodium and lithium could not be prepared.

The X-ray diffraction pattern of $K_2V_6O_{16}$ was indexed using the cell dimensions determined by BLOCK[7] and the formula for $1/d^2_{hkl}$ for the monoclinic system.[8]

In the pattern for $K_2V_6O_{16}$ *hkl* reflexions from the 100, 020 and 001 planes appeared. Lines appear at similar *d*-spacings in the patterns for the ammonium, rubidium and cesium compounds. It was tentatively assumed that the compounds were isostructural

TABLE 2.—MAJOR LINES OF ANHYDROUS HEXAVANADATES

| | $K_2V_6O_{16}$ | | $(NH_4)_2V_6O_{16}$ | | $Rb_2V_6O_{16}$ | | $Cs_2V_6O_{16}$ | |
|---|---|---|---|---|---|---|---|---|
| *hkl* | *I* | *d* | *I* | *d* | *I* | *d* | *I* | *d* |
| 100 | *m* | 7·62 | *vs* | 7·84 | *s* | 7·82 | *m* | 8·15 |
| 110 | *m* | 5·64 | *s* | 5·75 | *m* | 5·72 | *vw* | 5·75 |
| 001 | *vw* | 4·95 | *w* | 4·98 | | | *vw* | 5·00 |
| 020 | *vw* | 4·22 | *w* | 4·21 | *m* | 4·22 | *w* | 4·23 |
| $\bar{1}01$ | *w* | 3·91 | | | *m* | 3·99 | | |
| 200 | | | *m* | 3·91 | | | *s* | 4·07 |
| 210 | *m* | 3·46 | *s* | 3·55 | *vw* | 3·54 | *vs* | 3·68 |
| 201 | | | *m* | 3·26 | *m* | 3·24 | *m* | 3·32 |
| 021 | *s* | 3·20 | *m* | 3·21 | *s* | 3·21 | *m* | 3·24 |
| 121 | | | | | | | *m* | 3·09 |
| 211 | | | *w* | 3·04 | *m* | 3·02 | | |
| $\bar{2}01$ | *m* | 2·85 | *m* | 2·92 | *s* | 2·92 | *m* | 3·01 |
| $\bar{1}21$ | *m* | 2·87 | *m* | 2·90 | | | | |
| 220 | *m* | 2·81 | *m* | 2·87 | *s* | 2·87 | *m* | 2·95 |
| 300 | | | | | | | *s* | 2·72 |
| 002 | *w* | 2·47 | *w* | 2·49 | *s* | 2·49 | | |
| 310 | *w* | 2·42 | | | | | *s* | 2·59 |
| $\bar{2}21$ | *w* | 2·36 | *w* | 2·40 | *m* | 2·40 | | |
| $\bar{2}22$ | *w* | 1·78 | *w* | 1·80 | *m* | 1·80 | *m* | 1·83 |

TABLE 3.—CELL DIMENSIONS OF THE ANHYDROUS HEXAVANADATES
System: all monoclinic

| | $K_2V_6O_{16}$* | $(NH_4)_2V_6O_{16}$ | $Rb_2V_6O_{16}$ | $Cs_2V_6O_{16}$ |
|---|---|---|---|---|
| *a* | 7·63 | 7·87 | 7·85 | 8·21 |
| *b* | 8·43 | 8·43 | 8·43 | 8·43 |
| *c* | 4·97 | 5·01 | 5·01 | 5·04 |
| $\beta$ | 96°45′ | 96°45′ | 96°45′ | 96°45′ |

* Data of BLOCK[2]

and that these lines were due to reflexions from the same planes. Thus the cell dimensions *a*, *b* and *c* for these compounds could be estimated by making the assumption thar $\beta$ remains unchanged. Small changes in $\beta$ would not appreciably affect the calculation since $\beta$ is close to 90°.

These estimated cell dimensions were then corrected using higher orders of the *h*00, 0*k*0 and 00*l* reflexions. In all but one case at least one or two higher order reflexions were observed. In the case where higher order reflexions of one cell dimension were lacking a trial and error correction involving observed *hkl* reflexions was made. These

[8] L. V. AZAROFF and M. J. BUERGER, *The Powder Method*, p. 53. McGraw-Hill, New York (1958).

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accurate cell dimensions and the assumption that $\beta$ remains unchanged were then tested by comparing the observed and calculated values of $1/d^2_{hkl}$ for a number of the stronger reflexions. In each case good agreement was observed, indicating that the cell dimensions $a$, $b$, $c$ and $\beta$ had been properly selected. They are shown in Table 3.

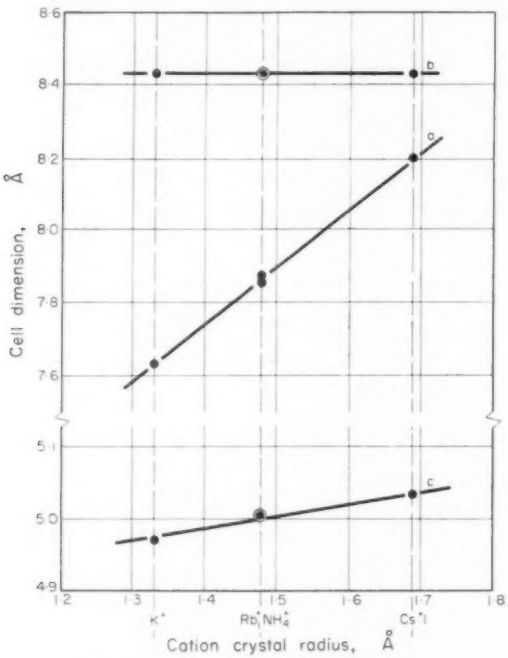


FIG. 1.—Cell dimension vs. cation radius.

All the lines in the diffraction patterns for ammonium, rubidium and cesium were indexed using the dimensions given in Table 2. Excellent agreement of the observed and calculated values of $1/d^2_{hkl}$ was obtained with the ammonium and rubidium compounds. The agreement in the case of cesium was good, but not quite as precise.

It was concluded that the potassium, ammonium, rubidium and cesium hexavanadates are isostructural. They undergo a linear expansion in the $a$ and $c$ dimensions as the ionic radius of the cation increases, as shown in Fig. 1. Sodium and lithium analogues were not obtained.

J. Inorg. Nucl. Chem., 1961, Vol 21, pp. 49 to 57. Pergamon Press Ltd. Printed in Northern Ireland

# ADDUCTS OF COPPER(II) β-DIKETONE CHELATES WITH HETEROCYCLIC BASES

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**Abstract**—Equilibrium constants have been determined at room temperature for the 1:1-addition of heterocyclic bases to copper(II) β-diketone chelates in three solvents. Irrespective of changes in the other two variables, the stability of the adducts increases in the order:

(a) 2:6:dimethyl-pyridine < 2:methyl-pyridine < pyridine < 4:methyl-pyridine
(b) acetylacetonate < benzoylacetonate < ethyl-acetoacetate
(c) chloroform < acetone < benzene

Variations of stability of the adducts due to changing bases are attributed in part to changes in donor power and in part to steric effects. Variations from one copper compound to another are related to the residual positive charges on the copper atoms of the chelates and solvent affects are thought to be due mainly to changes in the solvation energies of the bases.

The addition compounds $(CH_3CO{\cdot}CH{\cdot}CO_2C_2H_5)_2Cu(C_6H_7N)_2$, $(CH_3CO{\cdot}CH{\cdot}CO_2C_2H_5)_2Cu(C_5H_5N)_2$, $(C_6H_5CO{\cdot}CH{\cdot}COCH_3)_2Cu(C_6H_7N)$, $(C_6H_5CO{\cdot}CH{\cdot}COCH_3)_2Cu(C_5H_5N)$ and $(CH_3CO{\cdot}CH{\cdot}COCH_3)_2Cu(C_6H_7N)$ have been isolated by crystallisation of the β-diketonates from pyridine or 4:methyl-pyridine. Infra-red and visible region absorption spectra indicate a 5:co-ordinated structure for all of these compounds, the 1:2-adducts of bis(ethyl-acetoacetato)copper(II) having the additional molecule of heterocyclic base free in the crystal lattice. The magnetic properties of these adducts are normal, the moment of the copper atom being 1·81–1·85β.

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## 1. FORMATION CONSTANTS FOR 1:1-ADDUCTS

THE reaction of heterocyclic bases with chelate copper(II) β-diketone complexes (e.g. bis(acetylacetonato) copper(II)) in non-aqueous solutions produces 1:1-adducts,[1] their stoicheiometry being shown by a well defined isosbestic point and equilibrium constants of the form:

$$k = \frac{[\text{adduct}]}{[\text{diketonate}] \times [\text{base}]}$$

which are highly consistent over a wide range of composition. The identity of the absorption spectra of the simple chelates in solution in pure pyridine with the extrapolated spectra of the 1:1-adducts shows, moreover, that only one molecule of pyridine is added to the complexes even under these conditions.

Because of the comparatively low stability of the adducts ($k < 100$) these systems are particularly well suited for detailed examination by the spectroscopic method. In this paper we report the effect on the room-temperature (20–22°C) equilibrium constants of independent variation of the solvent, the heterocyclic base and the chelating ligand. Three copper compounds, bis(acetylacetonato) copper(II) (abbreviated in the tables to "$Cu(acac)_2$"), bis(benzoylacetonato) copper(II) ("$Cu(bzac)_2$") and bis(ethyl-acetoacetato) copper(II) ("$Cu(acest)_2$"), have been studied in conjunction with the four bases pyridine, 2:methyl-pyridine (α-picoline), 4:methyl-pyridine (γ-picoline) and 2:6:dimethyl-pyridine (2:6:lutidine). Some difficulty was experienced

[1] D. P. GRADDON, *Nature, Lond.* **183**, 1610 (1959).

in finding solvents of different types which would dissolve all of the copper compounds, the acetylacetonate being particularly insoluble, but adequate solubility was obtained using chloroform, acetone and benzene; bis(dibenzoylmethanato) copper(II) was found to be too insoluble, even in chloroform, for equilibrium studies to be made.

Experimental results are summarized in Tables 1–3. Details are given in the experimental section.

TABLE 1.—FORMATION CONSTANTS FOR ADDUCTS OF BIS(ETHYL-ACETOACETATO)COPPER(II) IN THREE DIFFERENT SOLVENTS (MOLES$^{-1}$)

| Solvent | Lutidine | α-Picoline | Pyridine | γ-Picoline |
|---|---|---|---|---|
| benzene | 1·2 | 9·6 | 29·0 | 58·7 |
| acetone | 1·6 | 2·9 | 15·6 | 16·0 |
| chloroform | 0·44 | 1·6 | 3·3 | 8·0 |

TABLE 2.—FORMATION CONSTANTS FOR THE ADDUCTS OF THREE COPPER COMPOUNDS IN CHLOROFORM SOLUTION (MOLES$^{-1}$)

| Cu-compound | Lutidine | α-Picoline | Pyridine | γ-Picoline |
|---|---|---|---|---|
| $Cu(acest)_2$ | 0·44 | 1·6 | 3·3 | 8·0 |
| $Cu(bzac)_2$ | 0·25 | 0·74 | 2·8 | 3·9 |
| $Cu(acac)_2$ | 0·23 | 0·66 | 2·0 | 2·7 |

TABLE 3.—FORMATION CONSTANTS OF PYRIDINE ADDUCTS OF THREE COPPER COMPOUNDS IN THREE DIFFERENT SOLVENTS (MOLES$^{-1}$)

| Cu-compound | Chloroform | Acetone | Benzene |
|---|---|---|---|
| $Cu(acest)_2$ | 3·3 | 15·6 | 29·0 |
| $Cu(bzac)_2$ | 2·8 | 7·5 | 21·6 |
| $Cu(acac)_2$ | 2·0 | 4·4 | 7·2 |

*Base effects*

Tables 1 and 2 show that for each copper compound and in each solvent the adduct formation constants increase in the order:

2:6:dimethyl-pyridine < 2:methyl-pyridine < pyridine < 4:methyl-pyridine.

The higher stability of the 4:methyl-pyridine adducts relative to those of pyridine reflects the increased donor property of the nitrogen atom due to substitution. A similar effect would be expected for substitution in the 2:position, so that the much lower stabilities observed for the adducts of 2:methyl-pyridine and 2:6:dimethyl-pyridine are probably due to steric interference. It thus seems likely that both energy and entropy factors are involved and we hope to confirm this by repeating our determinations at other temperatures.

These results parallel those observed by SACCONI *et al.*[2] for the addition of two molecules of heterocyclic bases to diacetyl-bis(benzoylhydrazone)nickel(II), except

[2] L. SACCONI, G. LOMBARDO and P. PAOLETTI, *J. Inorg. Nucl. Chem.* **8**, 217 (1958).

that in their experiments there was very little difference between the stabilities of the 2:methyl-pyridine and 2:6:dimethyl-pyridine adducts.

*Ligand effects*

Tables 2 and 3 show that, irrespective of which solvent or base is used, the stabilities of the adducts increase in the order:

$$Cu(acac)_2 < Cu(bzac)_2 < Cu(acest)_2$$

This is the order of decreasing stability of the copper compounds themselves[3] and resolution of the visible region absorption spectra in chloroform solution into Gaussian components shows that it is also the order of decreasing energy of the ligand-field transitions, which occur as follows:

| | | | |
|---|---|---|---|
| $Cu(acac)_2$ | 1·52 | 1·88 | $\mu^{-1}$ |
| $Cu(bzac)_2$ | 1·48 | 1·86 | $\mu^{-1}$ |
| $Cu(acest)_2$ | 1·45 | 1·80 | $\mu^{-1}$ |

(for discussions of the absorption spectra of these complexes see references 4, 5)

We should expect that the order of decreasing ligand-field effect would also be the order of decreasing transfer of negative charge from the ligand to the metal atom, and consequently of increasing residual positive charge on the metal atom; whence the increasing ability for further co-ordination.

*Solvent effects*

Tables 1 and 3 show the effects of solvent variation, the stabilities of the adducts increasing in the order chloroform < acetone < benzene.*

This effect could be produced by decreasing attraction between solvent molecules and the exposed copper atoms of the chelates or by decreasing solvation energy of the bases; between these two effects we might expect distinction to be difficult, but there is some evidence in favour of the latter alternative:

(a) The observed order of solvents is not the order of dipole moments or dielectric constants (in both cases benzene < chloroform < acetone), nor is it the order of the energy of ligand-field transitions, those of bis(ethyl-acetoacetato)copper(II), for example, occurring at the following frequencies in the visible region:

| | | | |
|---|---|---|---|
| Chloroform | 1·45 | 1·80 | $\mu^{-1}$ |
| Acetone | 1·40 | 1·70 | $\mu^{-1}$ |
| Benzene | 1·43 | 1·78 | $\mu^{-1}$ |

(b) Considerable heat was evolved when the heterocyclic bases were dissolved in chloroform, very little when the other solvents were used; this energy would have to be restored, at least partially, in the process of adduct formation, thus leading to lower formation constants.

* Except for a barely significant reversal of the acetone-benzene order in the system $Cu(acest)_2$-2:6-lutidine; however all of the experiments involving 2:6-lutidine give rather inaccurate values of $k$ due to the small extent of adduct formation.

[3] T. S. Moore and M. W. Young, *J. Chem. Soc.* 2694 (1932).
[4] R. C. Belford, M. Calvin and G. Belford, *J. Chem. Phys.* **26**, 1165 (1957).
[5] D. P. Graddon, *J. Inorg. Nucl. Chem.* **14**, 161 (1960).

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## 2. ISOLATION AND PROPERTIES OF SOLID ADDUCTS

By crystallisation of the copper II $\beta$-diketonates from solutions in pure heterocyclic bases we have obtained the following solid products:

From 4:methyl-pyridine: $(CH_3CO{\cdot}CH{\cdot}CO_2C_2H_5)_2Cu(C_6H_7N)_2$, $(C_6H_5CO{\cdot}CH{\cdot}COCH_3)_2Cu(C_6H_7N)$ and $(CH_3CO{\cdot}CH{\cdot}COCH_3)_2Cu(C_6H_7N)$; bis(dibenzoylmethanato)copper(II) recrystallized unchanged from this solvent.

From pyridine: $(CH_3CO{\cdot}CH{\cdot}CO_2C_2H_5)_2Cu(C_5H_5N)_2$ and $(C_6H_5CO{\cdot}CH{\cdot}COCH_3)_2Cu(C_5H_5N)$; bis(dibenzoylmethanato)copper(II) and bis(acetylacetonato)copper(II) crystallized unchanged from this solvent.

From 2:methylpyridine and 2:6:dimethyl-pyridine all four copper compounds recrystallized unchanged.

The crystals of bis(ethyl-acetoacetato)bis(4:methyl-pyridine)copper(II) were bright green; those of the other compounds were dark green in colour. All of these compounds decomposed on exposure to the air, losing the heterocyclic base as vapour and leaving a residue of the powdered $\beta$-diketonate. The rate of decomposition was variable, bis(ethyl-acetoacetato)bis(pyridine) copper(II) decomposing in a few minutes while bis(ethyl-acetoacetato)bis(4:methyl-pyridine)copper(II), the most stable of the adducts, required several hours for complete decomposition. This decomposition was apparently reversible, since all of the adducts could be preserved indefinitely in closed containers.

We were unable to obtain the 1:1-adducts of bis(ethyl-acetoacetato)copper(II) with either pyridine or 4:methyl-pyridine, either as intermediates in the decomposition of the 2:1-adducts or by combination of the bases with bis(ethyl-acetoacetato) copper(II) in a variety of solvents, and are led to believe that the second molecule of base in the 2:1-adducts is only filling spaces in the crystal lattice and not co-ordinated to the copper atom; this view is supported by the visible region absorption spectra discussed below.

We have also determined the magnetic moment of the copper atom in these compounds. The results, shown in Table 4, fall in the range usually observed for copper(II) compounds, indicating a single uncompensated spin and very small orbital contribution.

## 3. STRUCTURE OF THE ADDUCTS

Infra-red spectra of the solid adducts were examined in Nujol mulls, in which the adducts are shown to be stable by the corresponding visible region absorption spectra. In the rock-salt region these adducts all show the two very strong absorption bands between 1520–1600 $cm^{-1}$, which are characteristic of the chelate $\beta$-diketonate ring.[6]

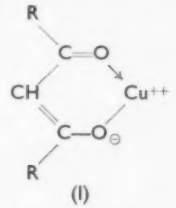
TABLE 4.—MAGNETIC PROPERTIES OF THE ADDUCTS

| Compound | Temp. (°C) | $10^6\chi$ | $10^6\chi M$ | $10^6\chi M$* | $\mu_{eff}$ |
|---|---|---|---|---|---|
| $Cu(acest)_2\gamma\text{-pic}_2$ | 17 | 2·45 | 1245 | 1475 | 1·85 |
| $Cu(acest)_2py_2$ | 20 | 2·55 | 1226 | 1432 | 1·84 |
| $Cu(bzac)_2\gamma\text{-pic}$ | 23 | 2·45 | 1175 | 1379 | 1·81 |
| $Cu(bzac)_2py$ | 20 | 2·59 | 1203 | 1385 | 1·81 |
| $Cu(acac)_2\gamma\text{-pic}$ | 17 | 3·57 | 1260 | 1413 | 1·82 |

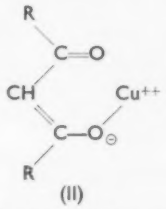
* Corrected for diamagnetism.

[6] A. WEISSBERGER (Editor) *Technique of Organic Chemistry*, Vol. 9, p. 494, Interscience, New York (1949).

The absence of any further absorption in the 1600–3000 $cm^{-1}$ range shows conclusively that the chelate rings remain closed (I) in the solid adducts, since the opening of one or both rings would not only cause weakening or disappearance of these bands but also the appearance of new bands in the 1600–1700 $cm^{-1}$ region, characteristic of the free, conjugated carbonyl group thus formed (II)




(I)



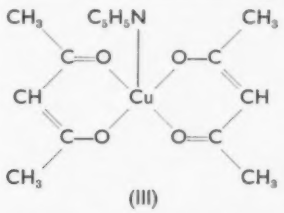

(II)

Visible region absorption spectra of the solid adducts dispersed in Nujol mulls were also examined. These spectra were quite different from those of dispersions of the copper(II) β-diketonates (Fig. 1), showing that the adducts were stable under these conditions. The spectra of the adducts showed a single, rather broad, band, the wavelengths of maximum extinction corresponding with those observed for solutions of the copper(II) β-diketonates in pure heterocyclic bases and with those calculated for the 1:1-adducts postulated as end-products in the equilibrium studies (Fig. 2). Since the visible region absorption is attributable to the ligand-field round the metal atom, we thus have evidence that the environment of the copper atom is the same in each of the three cases:

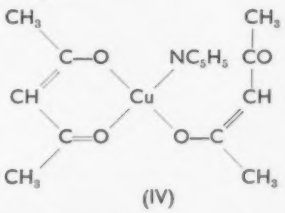
(a) in the solid adducts
(b) in the 1:1-adducts formed in solution
(c) in solutions in pure heterocyclic bases.

It thus appears that the solid 2:1-adducts formed by bis(ethyl-acetoacetato) copper(II) probably do not contain molecular species of this composition, but should rather be regarded as 1:1-adducts with an additional molecule of base occupying a vacant space in the crystal lattice; this conclusion is supported by our inability to isolate the intermediate 1:1-adducts and by our failure to observe the co-ordination of a second molecule of base in solution.

The 5:co-ordinated structure (III), in which the heterocyclic base is co-ordinated along the axis normal to the molecular plane of the copper compound, has been questioned by TRAILL.[7] who suggests as an alternative the 4:co-ordinated structure (IV), in which one of the chelate rings has been opened.




(III)




(IV)

We have discussed this suggestion, for which no experimental evidence is offered, elsewhere,[8] and, while final proof must await X-ray analysis of a solid adduct, we

[7] R. C. TRAILL, *Nature, Lond.* **186,** 631 (1960).
[8] D. P. GRADDON and E. C. WATTON, *Nature, Lond.* **187,** 1021 (1960).

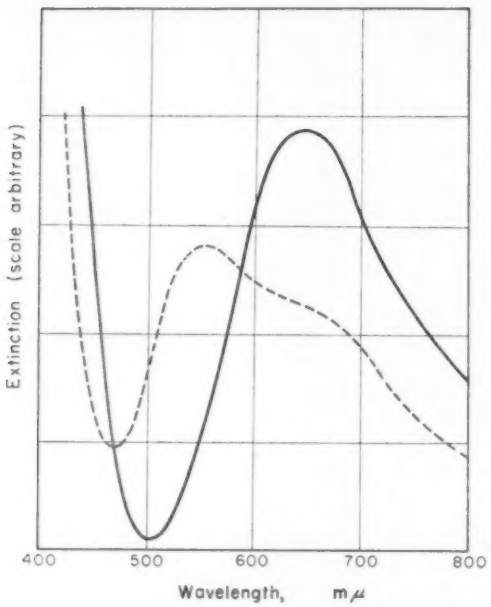



FIG. 1.—Absorption spectra of solid bis(benzoylacetonato)copper(II) (– – – – –) and its 4:methyl-pyridine adduct (———) in dispersions in Nujol.

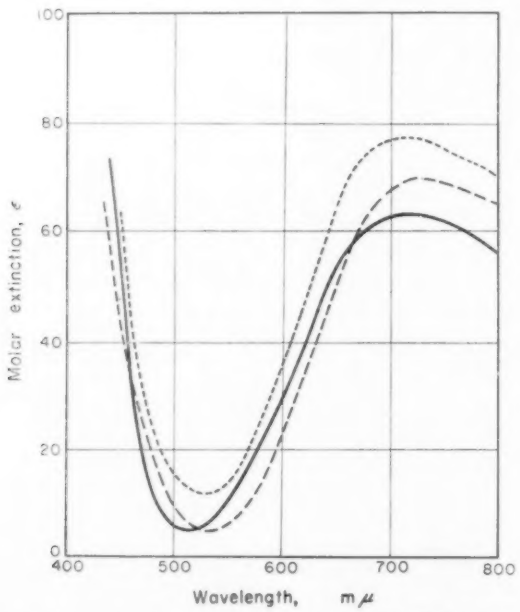



FIG. 2.—Absorption spectra of bis(ethyl-acetoacetato)copper(II) in 4:methyl-pyridine solution (– – – – –), of the product of reaction of bis(ethyl-acetoacetato)copper(II) with 4:methyl-pyridine in benzene solution (·····) and of solid bis(ethyl-acetoacetato)-bis(4:methyl-pyridine)copper(II) dispersed in Nujol (———). The extinction scale for this last spectrum is arbitrary.

believe that the available evidence strongly favours structure (III). The main points of this evidence are:

(1) the improbability of opening only one of the two chelate rings;

(2) the shift of the visible region absorption maximum to longer wavelength on addition of pyridine; replacement of an O-donor by an N-donor in the molecular plane (as in IV) would be expected to cause a shift to shorter wavelength;

(3) the major change in the Gaussian components of the visible region absorption[5] from two bands at about 1·4 and 1·8 $\mu^{-1}$ in the simple chelates to two bands at about 1·4 and 1·1 $\mu^{-1}$ in the adducts;

(4) the preservation with unchanged intensity in solutions of the adducts of the two very strong infra-red absorption bands between 1500–1600 $cm^{-1}$, which are characteristic of the chelate rings; and the above-mentioned infra-red spectra of the solid adducts.

We would further point out that as a result of recent X-ray analyses 5:co-ordination is now established in at least seven crystalline compounds, viz:—copper(II) selenite dihydrate,[9] tetrammine-copper(II) sulphate monohydrate,[10] bis(dimethylglyoximato)copper(II),[11] dichloro(dimethylglyoxime)-copper(II),[12] anhydrous cupric formate,[13] di-iodo-bis(dipyridyl)copper(II)[13] and the mineral $Cu_8Mg_8(CO_3)_4(OH)_{24}\cdot 8H_2O$.[14] Unsymmetrical 4:co-ordination of copper(II) is, on the other hand, very rare.

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## EXPERIMENTAL

*Materials.* Bis(acetylacetonato)copper(II), bis(benzoylacetonato)copper(II), bis(dibenzoylmethanato)copper(II) and bis(ethyl-acetoacetato)copper(II) were prepared by the reaction of equivalent quantities of cupric sulphate, sodium hydroxide and acetylacetone, benzoylacetone, dibenzoylmethane or ethyl acetoacetate in aqueous solution. The precipitated copper compounds were dried in vacuo; bis(ethyl-acetoacetato)copper(II) was recrystallized from benzene, the other compounds from glacial acetic acid.

Reagent grade heterocyclic bases were redistilled through a fractionating column, rejecting the first and last quaters of the distillate, then dried over potassium hydroxide. Analytical reagent grade solvents were dried over potassium carbonate.

*Spectrophotometric determination of equilibrium constants.* Absorption spectra and equilibrium constants were determined on a Unicam SP500 spectrophotometer at the prevailing room temperature in the range 20–22°C. Throughout the experiments 4 cm cells were used with a total copper concentration of 0·0025 gramme-atom per litre (with the sole exception of the reaction of bis(acetylacetonato)copper(II) in acetone solution, for which the copper concentration was halved on account of the low solubility of the compound). Extinctions of the bis(acetylacetonato)- and bis(benzoylacetonato)-copper(II) solutions were determined at 670 m$\mu$, those of bis(ethyl-acetoacetato)copper(II) solutions at 700 m$\mu$.

Equilibrium concentrations of the various species were calculated assuming a linear relationship between the observed extinction and the mole-fraction of the copper present as adduct:

$$[\text{adduct}] = [\text{total Cu}] \times \frac{\varepsilon - \varepsilon_0}{\varepsilon_\infty - \varepsilon_0}$$

where values of $\varepsilon$ and $\varepsilon_0$ were experimental and values of $\varepsilon_\infty$ were those found, by trial and error, to give the most reproducible values of the equilibrium constant, $k$.

[9] G. Gattow, *Acta Cryst.* **11**, 377 (1958).
[10] F. Mazzi, *Acta Cryst.* **8**, 137 (1955).
[11] E. Frasson, R. Bardi and S. Bezzi, *Acta Cryst.* **12**, 201 (1959).
[12] G. A. Barclay. Private communication (1960).
[13] G. A. Barclay and C. H. L. Kennard. Private communication (1960).
[14] G. D. Brunton, H. Steinfink and C. W. Beck, *Acta Cryst.* **11**, 169 (1958).

TABLE 5.—TYPICAL EQUILIBRIUM CONSTANT DETERMINATIONS

| Experimental details | $\varepsilon$ | Equilibrium concs. (mmole/l.) | | | $k$ (moles$^{-1}$) |
|---|---|---|---|---|---|
| | | Base | Adduct | Cu-cpd. | |
| Bis(ethyl-acetoacetato)copper(II) and 4:methyl-pyridine in benzene | 36·0 | 0·00 | 0·00 | 2·50 | — |
| | 45·0 | 5·67 | 0·58 | 1·92 | 53·3 |
| | 51·5 | 11·51 | 0·99 | 1·51 | 56·9 |
| | 60·0 | 23·46 | 1·54 | 0·96 | 68·4 |
| | 65·0 | 48·14 | 1·86 | 0·64 | 60·4 |
| Mean $k = 58·7 \pm 3·8$ | 69·0 | 97·88 | 2·12 | 0·38 | 57·0 |
| | 72·0 | 197·69 | 2·31 | 0·19 | 61·4 |
| | 73·5 | 497·59 | 2·41 | 0·09 | 53·8 |
| | 75·0 | ∞ | 2·50 | 0·00 | — |
| Bis(ethyl-acetoacetato)copper(II) and pyridine in benzene | 37·5 | 0·00 | 0·00 | 2·50 | — |
| | 47·5 | 11·82 | 0·68 | 1·82 | 31·6 |
| | 53·0 | 23·94 | 1·06 | 1·44 | 30·7 |
| | 56·0 | 36·23 | 1·27 | 1·23 | 28·5 |
| | 59·0 | 48·53 | 1·47 | 1·03 | 29·4 |
| Mean $k = 29·0 \pm 1·0$ | 64·0 | 98·18 | 1·82 | 0·68 | 27·3 |
| | 67·0 | 147·98 | 2·02 | 0·48 | 28·5 |
| | 70·0 | 297·77 | 2·23 | 0·27 | 27·7 |
| | 72·0 | 597·44 | 2·36 | 0·14 | 28·2 |
| | 74·0 | ∞ | 2·50 | 0·00 | — |
| Bis(benzoylacetonato)copper(II) and pyridine in acetone | 47·5 | 0·00 | 0·00 | 2·50 | — |
| | 57·0 | 49·32 | 0·68 | 1·82 | 7·57 |
| | 62·5 | 98·93 | 1·07 | 1·43 | 7·56 |
| | 65·5 | 148·71 | 1·29 | 1·21 | 7·17 |
| | 69·0 | 198·46 | 1·54 | 0·96 | 8·06 |
| Mean $k = 7·50 \pm 0·19$ | 71·5 | 298·29 | 1·71 | 0·79 | 7·26 |
| | 76·0 | 597·96 | 2·04 | 0·46 | 7·42 |
| | 77·5 | 797·86 | 2·14 | 0·36 | 7·46 |
| | 82·5 | ∞ | 2·50 | 0·00 | — |
| Bis(ethyl-acetoacetato)copper(II) and 2:methyl-pyridine in chloroform | 31·0 | 0·00 | 0·00 | 2·50 | — |
| | 32·5 | 24·90 | 0·10 | 2·40 | 1·67 |
| | 34·0 | 49·80 | 0·20 | 2·30 | 1·75 |
| | 36·0 | 99·67 | 0·33 | 2·17 | 1·53 |
| | 40·0 | 199·41 | 0·59 | 1·91 | 1·55 |
| Mean $k = 1·62 \pm 0·08$ | 43·0 | 299·21 | 0·79 | 1·71 | 1·54 |
| | 46·5 | 398·98 | 1·02 | 1·48 | 1·73 |
| | 50·5 | 598·72 | 1·28 | 1·22 | 1·75 |
| | 51·0 | 798·68 | 1·32 | 1·18 | 1·40 |
| | 54·0 | 998·45 | 1·55 | 0·95 | 1·63 |
| | 69·0 | ∞ | 2·50 | 0·00 | — |
| Bis(acetylacetonato)copper(II) and 2:6:dimethyl-pyridine in chloroform | 34·0 | 0·00 | 0·00 | 2·50 | — |
| | 34·5 | 49·97 | 0·03 | 2·47 | 0·24 |
| | 35·0 | 99·94 | 0·06 | 2·44 | 0·25 |
| | 35·5 | 149·91 | 0·09 | 2·41 | 0·25 |
| | 36·5 | 299·85 | 0·15 | 2·35 | 0·21 |
| Mean $k = 0·23 \pm 0·02$ | 39·0 | 599·70 | 0·30 | 2·20 | 0·23 |
| | 41·0 | 999·58 | 0·42 | 2·08 | 0·20 |
| | 76·0 | ∞ | 2·50 | 0·00 | — |

Table 5 shows the complete experimental results for five of the systems, including those with the highest and lowest values of $k$ and at least one example of each ligand, base and solvent. The average values of $k$ are given with 90 per cent confidence limits as an indication of the conformity of the equilibrium constants to the form:

$$k = \frac{[\text{adduct}]}{[\text{diketonate}] \times [\text{base}]}$$

*Preparation of adducts.* The adducts were prepared by crystallization of solutions of the cupric β-diketonates in pure heterocyclic bases; details of a typical experiment are as follows:

Bis(ethyl-acetoacetato)copper(II), 1·6 g, was dissolved in 10 ml of 4:methyl-pyridine warmed to about 30°C. On standing for a few hours green needles were formed; these were filtered, washed quickly with a little cyclohexane and dried at the pump. Yield 2·0 g (80% theoretical).

Analysis of product. Found: C 55·9, H 6·17, N 5·35, Cu 12·3%.
$C_{21}H_{32}O_6N_2Cu$ requires: 56·7 6·35 5·51 12·5%.

Analyses of the other adducts were as follows:

$Cu(acest)_2py_2$. Found: C 54·9, H 5·93, N 5·62, Cu 13·0%.
$C_{22}H_{28}O_6N_2Cu$ requires: 55·0 5·88 5·84 13·2%.
$Cu(bzac)_2\gamma$-pic. Found: C 64·7, H 5·00, N 2·99, Cu 13·6%.
$C_{26}H_{25}O_4NCu$ requires: 65·2 5·26 2·92 13·3%.
$Cu(bzac)_2$ py. Found: C 63·76, H 4·79, N 3·07, Cu 13·5%.
$C_{25}H_{23}O_4NCu$ requires: 64·57 4·99 3·01 13·7%.
$Cu(acac)_2\gamma$-pic. Found: C 53·4, H 5·68, N 4·00, Cu 17·6%.
$C_{16}H_{21}O_4NCu$ requires: 54·1 5·96 3·95 17·9%.

Visible-ultra-violet absorption spectra of the solid adducts were obtained on a Cary model 11 recording spectrophotometer as Nujol mulls spread on a rock salt diffusing disk and examined by transmitted light using a matched diffusing disk in the reference beam, according to the method of HARRIS *et al.*[15] Infra-red spectra were obtained in Nujol mulls on a double beam spectrometer using a Perkin–Elmer 12C monochromator.

*Acknowledgement*—We are grateful to Mr. I. H. REECE for infra-red and visible region spectra of the solid materials and to Dr. E. CHALLEN for microanalyses.

[15] C. M. HARRIS, S. E. LIVINGSTONE and I. H. REECE, *J. Chem. Soc.* 1505 (1959).

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# CHELATE COMPOUNDS OF TITANIUM WITH SALICYLALDEHYDE AND METHYL SALICYLATE

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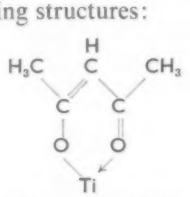
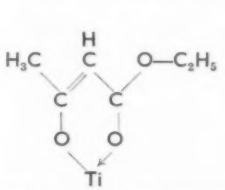
**Abstract**—The reactions of tetra-alkoxytitaniums with salicylaldehyde and methyl salicylate in a variety of molar ratios were studied and new penta-co-ordinated titanium compounds with three alkoxy groups and one chelating group (I and II) and a hexa-co-ordinated titanium compound with two alkoxy and two chelating groups were obtained. The infra-red spectra and the molecular weights of these chelate compounds were measured and the structures are discussed in comparison with acetylacetone- and ethyl acetoacetate-titanium chelate.

IN a previous paper[1] we reported the results of our study on the structures of the reaction products of tetraalkoxytitaniums with acetylacetone and ethyl acetoacetate. The reaction products were confirmed to have both alkoxy groups and chelate rings with the following ring structures:

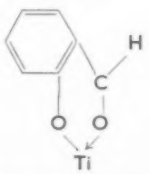



(acetylacetone chelate)

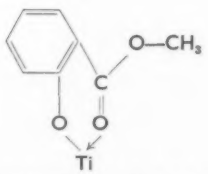



(ethyl acetoacetate chelate)

As corresponding aromatic chelating agents, salicylaldehyde and methyl salicylate have similar structures with a fused benzene ring in place of the enolic double bond of acetylacetone ane ethyl acetoacetate, and they were expected to form chelate rings of the following structures:




(salicylaldehyde chelate)




(methyl salicylate chelate)

Although titanium tetrachloride has been reported to form chelate compounds with salicylaldehyde and methyl salicylate,[2,3] no literature has been found concerning the reaction of tetra-alkoxytitaniums with these chelating agents. In the present study, the reactions of tetra-alkoxytitaniums with various molar ratios of salicylaldehyde and methyl salicylate were carried out, and the structures of the reaction products were studied by chemical and physical analyses.

[1] A. YAMAMOTO and S. KAMBARA, *J. Amer. Chem. Soc.* **79**, 4344 (1957).
[2] A. ROSENHEIM, *Ber. Dtsch. Chem. Ges.* **48**, 447 (1915).
[3] A. ROSENHEIM, O. SORGE, *Ber. Dtsch. Chem. Ges.* **53** B, 932 (1920).

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## EXPERIMENTAL

*Materials.* Tetraethoxy-, tetra-*n*-propoxy- and tetra-*n*-butoxy-titanium were prepared and purified as previously.[1] In each case satisfactory purity was indicated by chemical analysis of the compounds. Commercially available salicylaldehyde and methyl salicylate were purified by fractional distillation under reduced pressure; b.p. 92° (27 mm), $n_D^{25}$ 1·5709 for salicylaldehyde; b.p. 100° (16 mm), $n_D^{25}$ 1·5364 for methyl salicylate.

*Synthetic procedures.* Since the organic titanium compounds are very easily hydrolysed by moist air, care was taken to exclude moisture. Mixing, transfer and filtration were carried out in a dry box, the relative humidity of which was kept under 20 per cent. The syntheses were carried out on a 1/100 mole scale, and as the reactions are exothermic, appropriate solvents were used in some cases to dissipate the excess heat.

To 0·010 mole of a tetra-alkoxytitanium (tetraethoxy-, tetrapropoxy- and tetrabutoxy-titanium) was added 0·010 to 0·030 mole of salicylaldehyde or methyl salicylate at room temperature. With mixing of the two reactants heat was evolved and the mixture turned yellow immediately. Reactions were complete within 10 min and the solvents and alcohols formed as by-products were distilled off under reduced pressure. Since salicylaldehyde chelates are very susceptible to oxidation and tend to turn red in dry atmospheres containing oxygen, the distillation was carried out in a stream of nitrogen. The alcohol (ethyl, propyl and butyl alcohol) was identified in each case by measurement of refractive index. The chelated titanium compounds obtained as the distillation residue were pale yellow crystals or very viscous liquids, and the yield was quantitative in each case. They were purified by recrystallization from appropriate solvents or by distillation in a molecular still under high vacuum, keeping the bath temperature as low as possible to prevent heat decomposition.

*Molecular weight determinations.* Molecular weights were measured ebullioscopically in completely dried benzene. Modified KITSON type ebulliometer[4] equipped with thermister as thermosensitive element was used and the molecular elevation of benzene was calibrated with diphenyl as a reference.

*Ultra-violet absorption measurements.* These measurements were made with a Beckman DU spectrophotometer using 1·0 cm silica cells. The absorption spectrum of salicylaldehyde chelate $(C_2H_5O)_3Ti(OC_6H_4CHO)$ in ethyl alcohol solution was similar with that of salicylaldehyde having a strong absorption band at 39300 $cm^{-1}$ (255 m$\mu$). Methyl salicylate chelates are very unstable in ethyl alcohol solution and the absorption spectra could not be observed.

*The infra-red absorption measurements.* The infra-red measurements were carried out with a Perkin–Elmer recording spectrophotometer model 112 (single beam type). Liquid samples were measured in thin films and the solid samples were measured using Nujol.

TABLE 1.—PHYSICAL CONSTANTS AND ANALYTICAL DATA OF TITANIUM CHELATES

| No. | Formula | Appearance | M.p.* (°C) or Ref. Index† ($n_D^{25}$) | Analysis (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calc. | | | Found | | |
| | | | | Ti | C | H | Ti | C | H |
| 1 | $(H_5C_2O)_3Ti(OC_6H_4CHO)$ | Yellow prisms | 131–132 | 15·8 | 51·3 | 6·63 | 15·8 | 51·5 | 8·30 |
| 2 | $(H_7C_3O)_3Ti(OC_6H_4CHO)$ | Yellow prisms | 49–53 | 13·8 | 55·4 | 7·57 | 13·9 | 55·6 | 7·64 |
| 3 | $(H_9C_4O)_3Ti(OC_6H_4CHO)$ | Yellow prisms | 36–41 | 12·3 | 58·8 | 8·30 | 12·4 | 60·1 | 8·29 |
| 4 | $(H_5C_2O)_3Ti(OC_6H_4CO_2CH_3)$ | Light yellow prisms | 92–95 | 14·3 | 50·3 | 6·64 | 14·3 | 50·5 | 6·80 |
| 5 | $(H_5C_2O)_2Ti(OC_6H_4CO_2CH_3)_2$ | Light yellow viscous liquid | 1·612 | 10·9 | 54·6 | 5·49 | 10·9 | 54·7 | 5·51 |

* Melting points were measured in sealed capillary tubes.

† Measurement of refractive index was difficult on account of hydrolysis in air and the viscous nature of the compound.

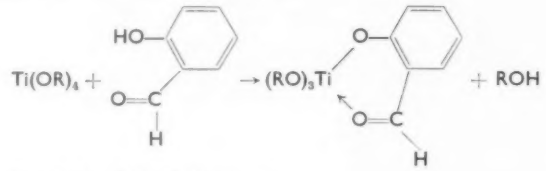
## RESULTS

(a) *Reactions of tetra-alkoxytitaniums with salicylaldehyde and methyl salicylate in a molar ratio of* 1:1. When equimolar amounts of salicylaldehyde and tetra-alkoxytitranium (tetraethoxy-, tetrapropoxy- and tetrabutoxy-titanium) were mixed at room

[4] R. E. KITSON, A. N. OMLER, J. MITCHELL, Jr., *Analyt. Chem.* **21**, 404 (1949).

temperature, heat was evolved and the reaction mixture turned yellow. From the reaction mixture one molar equivalent of an alcohol (ethyl, propyl and butyl alcohol) was distilled off and titanium chelates were obtained as crystals, as in the case of the reaction of a tetra-alkoxytitanium with acetylacetone. Physical constants and analytical data of purified compounds are summarized in Table 1 (Nos. 1, 2 and 3).

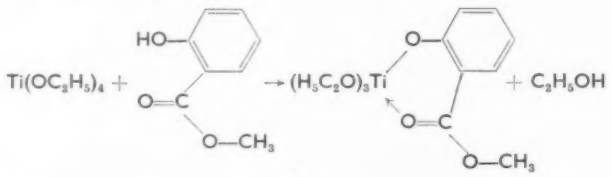
The results of the chemical analysis of the compounds obtained lead to structure I, which is considered to be formed by an exchange reaction of an alkoxy group of each tetra-alkoxytitanium with salicylaldehyde.




R = $C_2H_5$, $C_3H_7$, $C_4H_9$ I

These compounds are readily hydrolysed to gel-like materials in moist air, and the ease of hydrolysis increased with the alkyl chain length of the alkoxy groups attached to the titanium atom. The solubility in organic solvents such as benzene, alcohol, diethyl ether and petroleum ether also increased with the alkyl chain length, and appropriate solvents were selected for recrystallization.

In a similar experiment with tetraethoxytitanium and methyl salicylate, a pale yellow crystalline complex II and ethyl alcohol were obtained as in the case of the reaction of tetra-alkoxytitaniums with ethyl acetoacetate. Physical, and analytical data are shown in Table 1 (No. 4).




II

Molecular weights of I and II were determined in benzene solution ebullioscopically. The values are shown in Table 2. The observed values in dilute solutions are

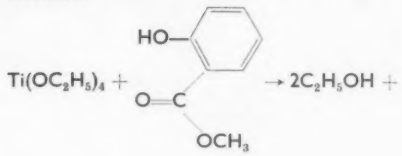
TABLE 2.—MOLECULAR WEIGHTS OF TRIETHOXYTITANIUM CHELATES DETERMINED BY EBULLIOMETER

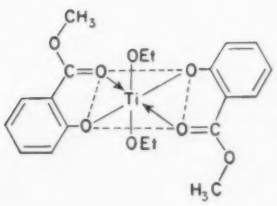
| Formula | Conc. (g/kg $C_6H_6$) | Mol. wt. | |
|---|---|---|---|
| | | Found | Calc. |
| $(H_5C_2O)_3Ti(OC_6H_4CHO)$ | 4·00 | 306 | 304 |
| | 9·80 | 344 | |
| | 15·53 | 362 | |
| | 24·14 | 390* | |
| $(H_5C_2O)_3Ti(OC_6H_4CO_2CH_3)$ | 3·09 | 343 | 334 |
| | 14·50 | 374* | |

* In more concentrated solution the determination was not possible because of the foaming of the boiling solutions.

closely consistent with the calculated values for penta-co-ordinated structure I and II and increase with concentration, indicating the association of the penta-co-ordinated complexes in concentrated solutions.

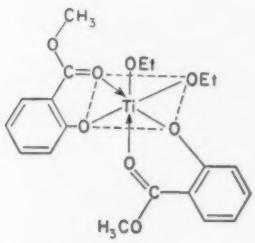
(b) *Reaction of tetra-alkoxytitaniums with salicylaldehyde and methyl salicylate in a molar ratio of* 1:2. In the case of the reaction of one mole of tetraethoxytitanium with two moles of methyl salicylate, two moles of ethyl alcohol and liquid product were obtained. From the chemical analysis of the product (see Table 1, No. 5) and the amount of the alcohol formed, the reaction is considered to proceed according to the equation below, forming hexa-co-ordinated bis-(methyl salicylate)-dialkoxytitanium (IIIa or IIIb), similar again to the reaction of tetra-alkoxytitaniums with ethyl aceto-acetate.




III a

or




III b

In the case of the reaction of one mole of tetra-alkoxytitaniums with two moles of salicylaldehyde, two moles of alcohols and intractable viscous liquid products were obtained. The liquid products were readily hydrolysed and oxidized in the air and purification could not be achieved by distillation or crystallization. In view of the amount of alcohols formed it is probable that similar compounds to III are formed in this case also.

When more than two moles of salicylaldehyde or methyl salicylate were used per mole of tetra-alkoxytitaniums, about two moles of the corresponding alcohol and the excess of the chelating agent were recovered. For example, in the case of the reaction of tetraethoxytitanium with methyl salicylate in a molar ratio 1:3, about two moles of ethyl alcohol and a small amount of methyl salicylate were recovered by distillation from the reaction mixture, leaving as residue a liquid product which when purified had a composition similar to III. It seems that one mole of a tetra-alkoxytitanium does not react with more than two moles of either chelating agent.

## DISCUSSION

*Infra-red spectra.* In Table 3 are listed the infra-red absorption maxima of $(H_5C_2O)_3Ti(OC_6H_4CHO)$ (I), $(H_5C_2O)_3Ti(OC_6H_4COOCH_3)$ (II) and $(H_5C_2O)_2Ti(OC_6H_4COOCH_3)_2$ (III). The spectrum of the (salicylaldehyde)-triethoxytitanium (I) has five strong absorption bands at 1040, 1064, 1102, 1123 and 1148 $cm^{-1}$. The spectra of (methyl salicylate)-triethoxytitanium (II) and bis-(methyl salicylate)-diethoxytitanium

TABLE 3.—INFRA-RED ABSORPTION BANDS OF I, II AND III. (WAVE NUMBERS IN $cm^{-1}$)

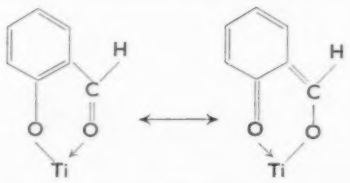
| I | II | III |
|---|---|---|
| 734 *w* | 706 *m* | 703 *s* |
| 764 *s* | 760 *s* | 760 *s* |
| 787 *m* | 841 *m* | 840 *s* |
| 862 *w* | 864 *w* | 864 *m* |
| 886 *m* | 879 *m* | |
| 904 *m* | 895 *m* | 896 *m* |
| 917 *m* | 915 *m* | 915 *sh* |
| 953 *w* | 954 *w* | 947 *w* |
| 1031 *sh* | | 1014 *m* |
| 1040 *s* | 1033 *s* | 1033 *s* |
| 1064 *vs* | 1065 *vs* | 1052 *m* |
| 1074 *sh* | | 1072 *m* |
| 1102 *vs* | 1094 *vs* | 1092 *vs* |
| 1123 *vs* | 1143 *s* | 1141 *m* |
| 1148 *vs* | 1160 *vs* | 1156 *s* |
| 1190 *m* | 1195 *sh* | 1214 *w* |
| 1209 *m* | 1243 *vs* | 1246 *vs* |
| | 1260 *sh* | 1260 *sh* |
| | | 1307 *m* |
| 1314 *vs* | 1327 *vs* | 1327 *vs* |
| 1373* *s* | 1376 *s* | 1377* *vs* |
| 1407* *s* | 1399 *m* | 1399 *m* |
| 1447* *m* | 1447 *s* | 1448* *s* |
| 1456* *s* | 1455 *sh* | 1458* *vs* |
| 1541 *m* | 1548 *s* | 1550 *s* |
| 1603 *m* | 1602 *s* | 1601 *s* |
| 1642 *vs* | 1630 *s* | 1634 *sh* |
| | 1651 *vs* | 1645 *vs* |
| | | 1651 *vs* |

Relative intensity: weak (*w*); medium (*m*); strong (*s*); very strong (*vs*); shoulder (*sh*). The spectra of I and II were measured in Nujol mull, III in thin film using a NaCl prism.

* These bands are obscured by overlapping of absorption bands of Nujol.

(III) are similar except for small differences and have also four to five strong bands in the region between 1000 and 1150 $cm^{-1}$. These bands correspond well with those of tetraethoxytitanium at 1040, 1054, 1101 and 1138 $cm^{-1}$. In view of the infra-red spectra of organic titanium compounds containing alkoxy and chelating groups[1,5] these bands are ascribed to the skeletal C—O and C—C stretching vibrations of ethoxy groups. These facts prove the existence of ethoxy groups in the compounds.

In the previous study concerning acetylacetone and ethyl acetoacetate chelates, the effect of metal chelate formation on the two CO absorption bands of the ligands were reported;[1] the C=O bands of the ligands shifted to lower frequency and the C—O




[5] A. YAMAMOTO, S. KAMBARA, *J. Amer. Chem. Soc.* **81**, 2663 (1959).

bands shifted higher as a result of chelate formation. Also for salicylaldehyde chelate a resonating structure similar to acetylacetone chelate can be considered,* and in fact similar shifts of the two CO bands are observed.

The bands of the salicylaldehyde chelate at 1314 and 1643 $cm^{-1}$ can be ascribed to the C—O and C=O bands shifted by the chelate formation. BELLAMY and BEECHER stated in their report[6] that for salicylaldehyde chelate no C—O absorption band was observed, but there exist distinct bands for salicylaldehyde itself and for its sodium chelate at 1276 and 1246 $cm^{-1}$ which can be ascribed to a C—O band.[7] Comparing the spectra of salicylaldehyde and its sodium chelate with the spectrum of the titanium chelate, the authors considered that it is reasonable to assign the band of salicylaldehyde -titanium chelate at 1314 $cm^{-1}$ to the C—O vibration, with increased double bond character owing to the resonance mentioned above.

The infra-red spectra of the methyl salicylate chelates are more complicated compared with the salicylaldehyde chelate. The pair of strong bands† between 1630 and 1651 $cm^{-1}$ are ascribed to the chelated C=O group, and one of the bands at 1327 $cm^{-1}$ and near 1243 $cm^{-1}$, probably the latter, to the chelated C—O bond. Further discussion of the infra-red spectra in comparison with acetylacetone and ethyl acetoacetate is presented in another paper.[9]

*Acknowledgements*—The authors wish to express their sincere thanks to Professor K. KOZIMA and Dr. H. YAMADA of Tokyo Institute of Technology for the infra-red spectra, and to Mr. NAKATA for his assistance. The authors are indebted to the Ministry of Education for financial support.

* Ionic resonating structures have to be considered in this case in addition to the structure shown here.

† Similar splitting is reported by DRYDEN and WINTER[8] for various $\beta$-diketone-titanium chelates.

[6] L. J. BELLAMY and L. BEECHER, *J. Chem. Soc.* **4491** (1954).
[7] H. YAMADA, *Bull. Chem. Soc. Japan* **32,** 105 (1959).
[8] R. P. DRYDEN and A. WINTER, *J. Phys. Chem.* **62,** 635 (1958).
[9] A. YAMAMOTO and S. KAMBARA, *J. Chem. Soc. Japan, Pure Chemistry Section* **80,** 1239 (1959).

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# THE THERMAL DECOMPOSITION OF SOME TETRAIODOMERCURATES

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(*Received* 28 *February* 1961)

**Abstract**—The thermal decomposition in air of the tetraiodomercurates of copper (I), silver (I), mercury (I), thallium (I), and lead (II) was studied on the thermal balance up to 1350°C. The thermal decomposition of the series falls into four classes: (1) for silver: decomposition to the metal; (2) for copper and lead: decomposition to the oxide; (3) for mercury: complete volatilization; and (4) for thallium: decomposition of the cationic metal to the iodide with subsequent volatilization. The thermochromic transition temperature of the thallium compound has been determined.

WATER-INSOLUBLE metal tetraiodomercurates are formed only by the coinage metals (Periodic Group IB) and those metals which immediately follow gold in the Periodic Table, that is, mercury, thallium, lead, and bismuth.[1] For bismuth, however, a compound of indefinite composition best formulated as $Bi(OH)HgI_4$ is formed.[1] They are all intensely coloured, very insoluble compounds which are, with the exception of the indefinite bismuth compound and possibly the gold compound, best known to exist as thermochromic enantiotropes, i.e. possess a reversible colour change at a definite temperature. Usually the transition temperature is extremely sharp, comparable to a melting point (which is another type of thermal enantiotropic transition). Table 1 lists the thermochromic enantiotropic transition temperatures (in air) of the compounds studied in this work.

All the above compounds are readily formed by the simple addition of an aqueous solution of potassium tetraiodomercurate (II) to an aqueous solution of the metal ion. In the case of copper, however, part of the precipitant will act as a reductant unless prior reduction to the univalent state is performed before-hand. This is due to the thermodynamic incompatibility of iodide and copper (II) ions and, perhaps, is an

TABLE 1.—THERMOCHROMIC ENANTIOTROPIC TRANSITION TEMPERATURES

| Compound | Transition temp. (°C) | Colour change | Reference |
|---|---|---|---|
| $Cu_2HgI_4$ | 71·0 | Red to black | 1, 2, 3, this work |
| $Ag_2HgI_4$ | 45–52* | Yellow to red | 1, 2, 3, this work |
| $Hg_2HgI_4$ | 172·6 | Yellow-orange to red | 1 |
| $HgHgI_4(HgI_2)$ | 126·3 | Scarlet to yellow | 2, 3 |
| $Tl_2HgI_4$ | 187·0 ± 1·0 | Orange to scarlet | This work |
| $PbHgI_4$ | 133·8 | Orange-red to yellow | 1 |

* The thermochromic transition temperature for this compound appears to vary from sample to sample for some unknown reason. There is much disagreement in the literature[1,2,3] on the true temperature. The sample used in this study had a thermochromic transition temperature of 45·0°C.

†Present address: Cornell Aeronautical Laboratory, Inc., 4455 Genesee Street, Buffalo 21, New York.

[1] M. MEYER, *J. Chem. Educ.* **20**, 145 (1943).
[2] W. R. HENDERSON and W. C. FERNELIUS, *A Course in Inorganic Preparations*, p. 148. McGraw-Hill, New York (1935).
[3] C. H. BACHMAN and J. B. MAGINNIS, *Amer. J. Phys.* **19**, 424 (1951).

indication of the relative stability of the tetraiodomercurate (II) complex. As a result, copper (II) tetraiodomercurate (II) does not exist.

Since all the compounds are formed in nearly quantitative yields and are all very insoluble, they lend some applicability to gravimetric analysis. A knowledge of their thermal stabilities should be quite useful.

## EXPERIMENTAL

All reagents used in this work were of A.R. grade or equivalent. The tetraiodomercurates were prepared in nearly quantitative yields (i.e. 99·8 per cent or better) by well established methods. The copper (I) salt was prepared by the method of WALTON[4] whereby an aqueous solution of copper (II) sulphate is reduced with sulphur dioxide at room temperature in the presence of a stoicheiometric amount of potassium tetraiodomercurate (II). The bright red precipitate was immediately filtered, washed with distilled water, and dried in a vacuum desiccator at room temperature. (Found: Cu (electrolytically) 15·2; Hg (thiocyanate titration) 23·8; I (iodometrically) 60·9. Calc. for $Cu_2HgI_4$: Cu, 15·2; Hg, 24·1; I, 60·7%).

The silver (I) salt was prepared by the method of HENDERSON and FERNELIUS[2], the mercury (I) and lead (II) salts by the method of MEYER[1], and the thallium (I) salt by the method of BARLOT and PERNOT[5]. These methods are identical in that a stoicheiometric amount of an aqueous solution of potassium tetraiodomercurate (II) is added to an aqueous solution of the respective nitrate at room temperature. The highly coloured precipitates are then treated as described above for the copper (I) salt. (Found: Ag (thiocyanate titration), 23·6; Hg, 21·2; I, 54·9. Calc. for $Ag_2HgI_4$: Ag, 23·4; Hg, 21·6; I, 55·0. Found: Hg, 54·1; I, 44·9. Calc. for $Hg_2HgI_4$: Hg, 54·3; I, 45·7. Found: Tl (gravimetrically as the chromate from alcoholic solution), 36·5; Hg, 17·6; I, 45·4. Calc. for $Tl_2HgI_4$: Tl, 36·6; Hg, 18·0; I, 45·4. Found: Pb (gravimetrically as the sulphate), 21·8; Hg, 22·3; I, 54·9. Calc. for $PbHgI_4$: Pb, 22·6; Hg, 22·0; I, 55·5%).

A Stanton Thermobalance, Model HT–1400, with a platinum wound furnace having a maximum temperature of 1420°C was used in this study. A heating rate of 5·5°C per min was employed. The samples were contained in a 5 ml recrystallized alumina crucible. In order to make the final interpretations easier, a millimole (0·001 mole) of each compound was used. Any loss or gain in weight could therefore be directly correlated to the molecular weight without further calculation. The weight losses were within 2 per cent of the theoretical values.

A Fisher-Johns melting point apparatus was used to determine the thermochromic transition temperature of $Tl_2HgI_4$. The instrument was standardized with a purified sample of $Cu_2HgI_4$.

## RESULTS AND DISCUSSION

The thermal decomposition curves of the metal tetraiodomercurates are shown in Figs. 1 and 2. The interpretation of each curve follows.

### *Copper (I) tetraiodomercurate (II)*, $Cu_2HgI_4$

The thermal decomposition curve for copper (I) tetraiodomercurate (II) is given in Fig. 1A. This compound is stable to 220°C where decomposition to copper (I) iodide and volatile mercury (II) iodide begins. Before the mercury (II) iodide is completely volatilized, air oxidation of the copper (I) iodide to copper (II) oxide commences at about 450°C. From 600 to 1050°C a horizontal level is found which corresponds to CuO. Beyond 1050°C decomposition of copper (II) oxide to copper (I) oxide occurs, the latter being stable to at least 1350°C. This change to the lower oxide at 1050°C is also expected from purely thermodynamic considerations. With the sole exception of the conversion of copper (II) oxide to copper (I) oxide, the observed thermal stabilities of copper (I) iodide and copper (II) oxide are in exact agreement with DUVAL[6] who used a maximum temperature of only 1000°C.

[4] H. R. WALTON, *Inorganic Preparations* p. 81. Prentice-Hall, New York (1948).
[5] J. BARLOT and J. PERNOT, *C.R. Acad. Sci., Paris* **173,** 232 (1921).
[6] C. DUVAL, *Inorganic Thermogravimetric Analysis*, pp. 237–273. Elsevier, New York (1953).



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*Silver (I) tetraiodomercurate (II)*, $Ag_2HgI_4$

The thermal decomposition curve for silver (I) tetraiodomercurate (II) is given in Fig. 1B. This compound exhibits remarkable thermal stability considering the fact that silver iodide is thermally stable only to 552°C and mercury (II) iodide begins to sublime at 130°C. Reference to the thermal decomposition curve shows that $Ag_2HgI_4$ is stable to 900°C where rapid evolution of iodine and mercury (II) iodide and/or mercury and iodine begins. At 1330°C only a silver residue remains which is stable to at least the upper temperature limit of the thermobalance.

*Mercury (I) tetraiodomercurate (II)*, $Hg_2HgI_4$

The thermal decomposition curve for mercury (I) tetraiodomercurate (II) is given in Fig. 1C. This compound exhibits the degree of thermal stability expected for a compound composed entirely of mercury and iodine. It is thermally stable to 120°C where volatilization commences. At 340°C, the recorded boiling point of mercury (II)

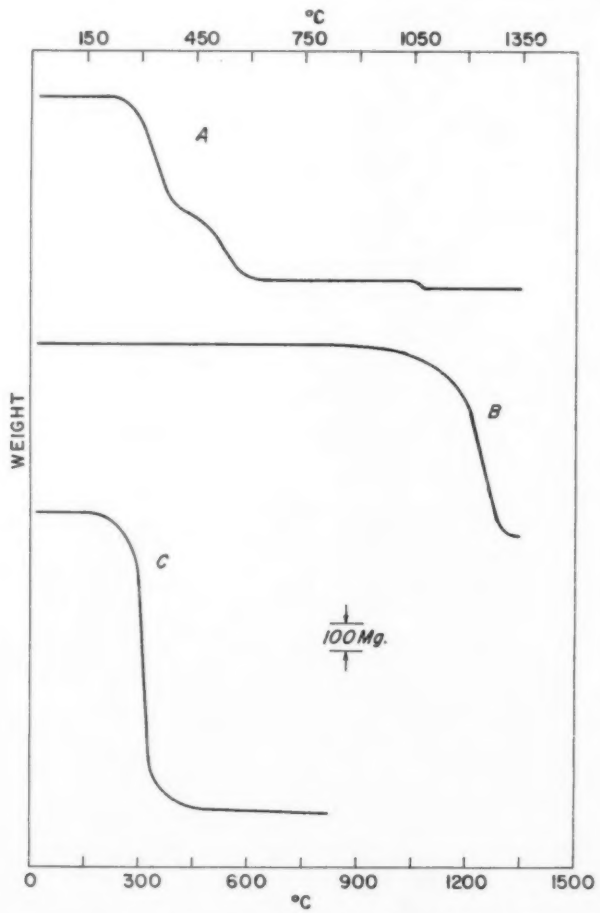


FIG. 1.—Thermogravimetric decomposition curves of (A) $Cu_2HgI_4$, (B) $Ag_2HgI_4$, and (C) $Hg_2HgI_4$.

iodide, the volatilization is virtually complete and levels off rapidly to complete volatilization at 460°C.

*Thallium (I) tetraiodomercurate (II)*, $Tl_2HgI_4$

The decomposition curve of thallium (I) tetraiodomercurate (II) is given in Fig. 2A. The thallium (I) salt is thermally stable to 225°C, at which point mercury (II) iodide begins to sublime, leaving a residue of thallium (I) iodide. At 560°C the vapour-pressure of thallium (I) iodide becomes appreciable and a noticeable loss of

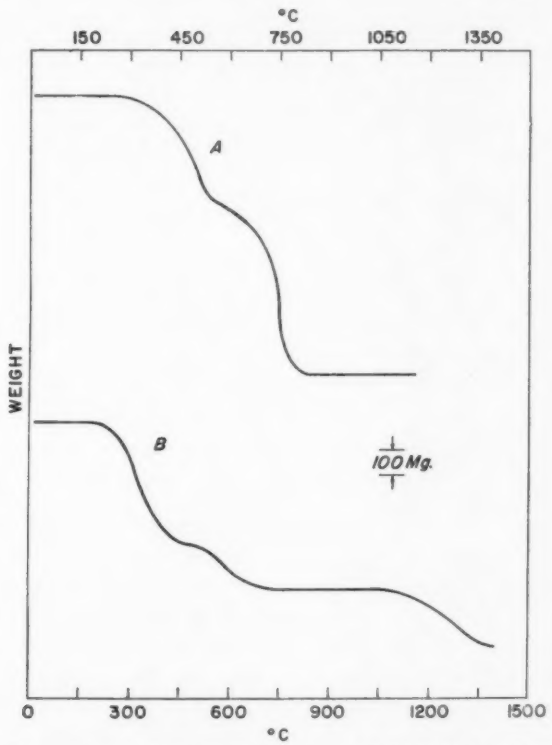


FIG. 2.—Thermogravimetric decomposition curves of (A) $Tl_2HgI_4$ and (B) $PbHgI_4$.

weight is observed. At the recorded boiling point of thallium (I) iodide, 825°C, the volatilization is complete and no residue remains.

*Lead (II) tetraiodomercurate (II)*, $PbHgI_4$

The thermal decomposition of lead (II) tetraiodomercurate (II) is given in Fig. 2B. This salt is stable to 180°C where mercury (II) iodide begins to volatilize, leaving a residue of lead (II) iodide; the small horizontal level observed from 450 to 510°C corresponds to lead (II) iodide. At the latter temperature this compound is converted to lead (II) oxide; the observed level area of the curve between 750 and 975°C corresponds to this compound. The recorded melting point of lead (II) oxide is 888°C so that at the high temperature portion of this horizontal the residue is present as a liquid which appears to begin to slowly volatilize at 975°C. At 1350°C the residue is

over 95 per cent volatilized, indicating that the boiling point of lead (II) oxide may be somewhat lower than the recorded value of 1472°C.[7]

## CONCLUSIONS

For analytical purposes, all the compounds save that of mercury (I) could be dried in a conventional drying oven at 105–110°C. The mercury (I) salt should be dried in a vacuum desiccator at room temperature, as done in this study, to ensure a constancy of composition. Prolonged heating for 2 hr of each of the other salts at 105–110°C showed that constant weight was obtained with no detectable decomposition. The silver salt has also been rapidly dried at the full heat of a Bunsen burner without a change in composition. Table 2 summarizes the thermal stabilities of the five compounds.

TABLE 2.—THERMAL STABILITY RANGES

| Compound | Decomposition temperature (°C) | Residue |
|---|---|---|
| $Cu_2HgI_4$ | 220 | $Cu_2I_2$ |
| | 450 | CuO |
| | 1050 | $Cu_2O$ |
| $Ag_2HgI_4$ | 900 | Ag |
| $Hg_2HgI_4$ | 120–460 | Volatilization, rapid over 200°C. |
| $Tl_2HgI_4$ | 225 | TlI |
| | 560–825 | Volatilization |
| $PbHgI_4$ | 180 | $PbI_2$ |
| | 510 | PbO |
| | 975–1350 | Volatilization |

All these compounds may be quantitatively precipitated by adding an aqueous solution of potassium tetraiodomercurate (II) to an aqueous solution of the respective metal nitrate at room temperature. The freshly precipitated compounds are ready for filtering immediately on a glass frit crucible of medium porosity. Each compound has a favourable gravimetric factor (i.e. substance sought/substance weighed) with respect to the cationic metal except the mercury (I) salt. These factors are: $2Cu/Cu_2HgI_4$, 0·1523; $2Ag/Ag_2HgI_4$, 0·2338; $3Hg/Hg_2HgI_4$, 0·5430; $2Tl/Tl_2HgI_4$, 0·3760; and $Pb/PbHgI_4$, 0·2265. If only the precipitated mercury (I) is considered in calculating the gravimetric factor for $Hg_2HgI_4$, it then becomes 0·3620, a more favourable figure. The combination of low aqueous solubility, ease of filtration, ease of drying at low temperatures, and favourable gravimetric factors indicates that appropriate gravimetric procedures could be developed using these compounds.

[7] K. K. KELLEY, U.S. Bureau of Mines Bulletin 383, p. 60 (1935).

J. Inorg. Nucl. Chem., 1961, Vol. 21, pp. 69 to 76. Pergamon Press Ltd. Printed in Northern Ireland

# THE THERMAL DECOMPOSITION OF METAL COMPLEXES—I

## THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS STUDIES

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**Abstract**—The thermal decomposition of a number of cobalt (III) amine complexes, several of them containing the carbonate ion in the coordination sphere, and several metal oxalato complexes were studied by the methods of TGA and DTA. The thermal stability of the carbonate complexes, as determined by the above methods, was: $[Co(NH_3)_4CO_3]NO_3 < [Co(tn)_2CO_3]Cl < [Co(pn)_2CO_3]Cl < [Co(en)_2CO_3]Cl$. For the metal oxalato complexes, the thermal stability order, based on DTA dehydration peak maxima, was: $K_3[Cr(C_2O_4)_3]\cdot 3H_2O < K_3[Co(C_2O_4)_3]\cdot 4H_2O = trans\text{-}K[Cr(C_2O_4)_2(H_2O)_2]\cdot 3H_2O < cis\text{-}K[Cr(C_2O_4)_2(H_2O)_2]\cdot 2H_2O = K_3[Rh(C_2O_4)_3]\cdot 2.5H_2O$. The thermal decomposition process for all of the complexes is discussed.

THE thermal properties of only a few of the many known cobalt (III) complexes have been studied by the methods of thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Previous studies on this subject have been carried out by ABLOV and co-workers,[1–3] WENDLANDT,[4] DUVAL,[5] GOLOVNYA and KOKH,[6] PARIS,[7] JOYNER and VERHOEK,[8] KYUNO,[9] KEKEDY *et al.*,[10] BOULLÉ and DOREMIEX,[11] OCONE *et al.*[12] FIZLARZ,[13] and MORI and co-workers.[14,15]

Although the thermal decomposition of a number of metal oxalates has been studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA),[16–22] no such studies have been made on the metal oxalato type complexes.

[1] A. V. ABLOV and N. I. LOBANOV, *Zh. Obshchĭ Khim.* **25**, 648 (1955).
[2] A. V. ABLOV, E. V. POPA and T. A. MAL'KOVA, *Zh. Neorg. Khim.* **1**, 2716 (1956).
[3] N. I. LOBANOV, I. S. RASSONSKAYA and A. V. ABLOV, *Zh. Neorg. Khim.* **3**, 1355 (1958).
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[5] C. DUVAL, *Inorganic Thermogravimetric Analysis*, Chap. 26. Elsevier, Amsterdam (1953).
[6] V. A. GOLOVNYA and L. A. KOKH, *Zh. Neorg. Khim.* (Eng. trans.) **5**, 27 (1960).
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[10] L. KEKEDY, A. SZURKOS, P. KROBL and E. KEKEDY, *Acad. Rep. Populare Romine, Filiala Cluj, Studii Cercetări Chim.* **9**, 79 (1958).
[11] A. BOULLÉ and J. L. DOREMIEUX, *C. R. Acad. Sci., Paris* **248**, 2211 (1959).
[12] L. R. OCONE, J. R. SOULEN and B. P. BLOCK, *J. Inorg. Nucl. Chem.* **15**, 76 (1960).
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[15] M. MORI, R. TSUCHIYA and Y. OKANO, *Bull. Chem. Soc. Japan* **32**, 1029 (1959).
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[17] Y. A. UGAI, *Zh. Obshchei Khim.* **24**, 1315 (1954).
[18] W. W. WENDLANDT, *Analyt. Chem.* **30**, 58 (1958); **31**, 408 (1959).
[19] W. W. WENDLANDT, T. D. GEORGE and G. R. HORTON, *J. Inorg. Nucl. Chem.* **17**, 273 (1691).
[20] C. DUVAL, *Inorganic Thermogravimetric Analysis*, Elsevier, Amsterdam (1953).
[21] V. M. PADMANABHAN, S. C. SARAIYA and A. K. SANDARAM, *J. Inorg. Nucl. Chem.* **12**, 356 (1960).
[22] K. V. KRISHNAMURTY and G. M. HARRIS, *Chem. Rev.* In press.

In this investigation, the thermal properties of several cobalt (III) complexes containing the carbonate ion in the co-ordination sphere, and the oxalato complexes of chromium (III), iron (III), cobalt (III) and rhodium (III), were investigated by the techniques of TGA and DTA.

## EXPERIMENTAL

### *Thermobalances*

*Thermobalance I.* This automatic recording instrument and its modification has previously been described.[23] Sample sizes ranged in weight from 50 to 75 mg. The furnace heating rate was approximately linear with time at 5°C per min with an air atmosphere maintained in the furnace.

*Thermobalance II.* This instrument consisted of a chainomatic analytical balance to which was attached a Fisher Recording Balance Attachment. A Moseley, Model 5S, X-Y recorder was used to record the balance attachment output. The weight change was recorded on the vertical axis while the temperature, as detected by a chromel–alumel thermocouple located in the furnace chamber, was recorded on the horizontal axis. The furnace and temperature controller were of the same type as previously described.[23] Sample sizes and heating rate were the same as the above instrument.

### *Differential thermal analysis apparatus*

*DTA I.* The apparatus has previously been described by LODDING and HAMMELL.[24] The sample and reference chambers consisted of ceramic cylinders, 0·25 in. in diameter and 0·75 in. in length fitted with chromel–alumel thermocouples to detect the differential temperatures. The e.m.f. output from the thermocouples was amplified by a Beckman, Model 14, breaker-type d.c. amplifier and recorded on the vertical axis of a Moseley, Model 5S, X-Y recorder. The differential temperature was plotted as a function of the temperature of the inert reference chamber. Sample sizes ranged in weight from 90 to 110 mg, with previously ignited α-alumina being used in the reference chamber. The samples were finely powdered and loosely packed in the sample holder by gentle tamping with a glass rod. Since the amount of sample was small compared to the volume of the sample holder, the remainder of the cylinder was filled with α-alumina. The furnace heating rate was approximately linear with time at about 10°C per min.

*DTA II.* This instrument consisted of a furnace, furnace temperature controller and sample holder similar to that previously described.[24] The differential temperature was recorded on a microvolt strip-chart recorder[25] instead of an X-Y recorder. The sample sizes and heating rate were the same as the DTA I unit.

### *Preparation of metal complexes*

Both $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ and $K_3[Co(C_2O_4)_3]\cdot 4H_2O$ were prepared by published methods for the *tris*-oxalato complexes;[26] the composition was checked by standard analytical methods.[27] The iron complex, $K_3[Fe(C_2O_4)_3]$, was prepared from the 3-hydrate.[26]

The rhodium complex, $K_3[Rh(C_2O_4)_3]\cdot 4.5H_2O$, was prepared by dissolving freshly precipitated $Rh(OH)_3$ in a $KHC_2O_4$ solution followed by slow crystallization to yield orange-red crystals[28,29] of the complex. Analytical determination of Rh, K and $C_2O_4$ contents agreed well with the above formula.

The *trans*-$K[Cr(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$ and *cis*-$K[Cr(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$ were prepared by WERNER's method,[30] starting with $K_2Cr_2O_7$ and $H_2C_2O_4\cdot 2H_2O$. The composition of both of these salts was found to agree well with their respective formulas.[31]

[23] W. W. WENDLANDT, *Analyt. Chem.* **30**, 56 (1958); **32**, 848 (1960).
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The $[Co(en)_2CO_3]Cl$ was prepared by boiling *trans*-$[Co(en)_2Cl_2]Cl$[32] with a stoicheiometric amount of aqueous $Na_2CO_3$.[33]

The $[Co(tn)_2CO_3]Cl \cdot H_2O$ was prepared from *trans*-$[Co(tn)_2Cl_2]Cl$[34] according to a modified procedure developed by BOYLE and HARRIS.[35]

The $[Co(en)_3]Cl_3$ was prepared as previously described[32] starting from cobalt chloride and ethylenediamine. The 2-hydrate was obtained from the anhydrous material by exposure to the atmosphere for 2–4 hr.

The $[Co(tn)_3]Cl_3$ was prepared according to the procedure of BAILAR and WORK[34] starting from cobalt chloride and trimethylenediamine, (tn), in the presence of animal charcoal as a catalyst.

The $[Co(pn)_2CO_3]Cl \cdot H_2O$ was prepared from *cis*-$[Co(pn)_2Cl_2]Cl$[36] by first aquating the latter for 12 hr and then triturating it with $Ag_2CO_3$ for about 1 hr. The solution, after removal of AgCl, was concentrated by evaporation to yield crystals of $[Co(pn)_2CO_3]Cl \cdot H_2O$.[37]

The $[Co(NH_3)_4CO_3]NO_3 \cdot 1H_2O$ was prepared according to JORGENSEN's procedure.[38]

The $[Co(en)_2C_2O_4]Cl \cdot H_2O$ was prepared by the method of BAILAR and AUTEN[39] starting from *cis*-$[Co(en)_2Cl_2]Cl$ and $Ag_2C_2O_4$.

## RESULTS AND DISCUSSION

*TGA studies on cobalt ammine complexes.* The TGA curve of the cobalt ammine complexes, as determined by thermobalance I, are given in Figs. 1 and 2.

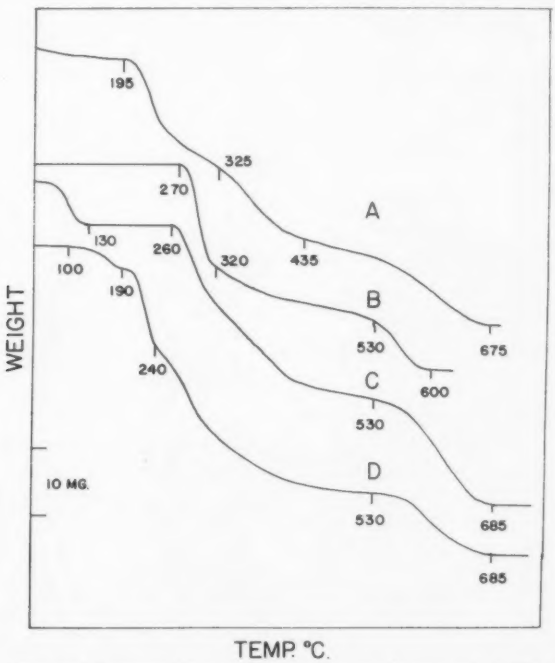


FIG. 1.—Thermal decomposition weight-loss curves of some cobalt (III) complexes. Thermobalance I.
*A*. $[Co(tn)_3]Cl_3$; *B*. $[Co(en)_2CO_3]Cl_3$; *C*. $[Co(en)_3]Cl_3 \cdot 2H_2O$; *D*. $[Co(tn)_2CO_3]Cl \cdot H_2O$.

[32] J. C. BAILAR, *Inorganic Syntheses* (Edited by W. C. FERNELIUS), Vol. 2, p. 223. McGraw-Hill, New York (1946).
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[35] J. E. BOYLE and G. M. HARRIS, *J. Amer. Chem. Soc.* **80**, 782 (1958).
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[38] S. M. JORGENSEN, *Z. Anorg. Chem.* **2**, 291 (1892).
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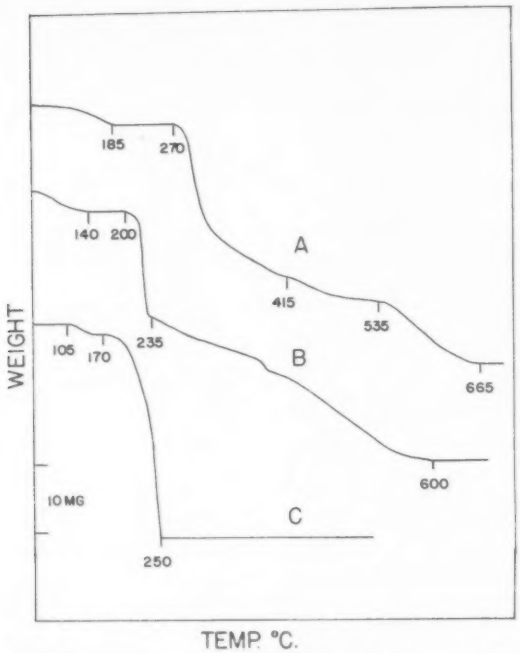


FIG. 2.—Thermal decomposition weight-loss curves of some cobalt (III) complexes. Thermobalance I.
*A*. $[Co(en)(C_2O_4)_2]Cl{\cdot}H_2O$; *B*. $[Co(pn)_2CO_3]Cl{\cdot}H_2O$; *C*. $[Co(NH_3)_4CO_3]NO_3{\cdot}H_2O$.

In all of the complexes studied, with the exception of $[Co(pn)_2CO_3]Cl{\cdot}H_2O$, the water of hydration was evolved at around 100° C. In the case of the latter, the water of hydration began to come off at room temperature or at temperatures slightly above this. The anhydrous metal complexes were obtained in the 130–190°C temperature range; the former value is for $[Co(en)_3]Cl_3{\cdot}2H_2O$, and the latter for $[Co(tn)_2CO_3]$-$Cl{\cdot}H_2O$. However, in the case of the latter compound, a horizontal weight level was not obtained so that the composition of the curve which corresponded to the anhydrous complex may be fortuitous. The amount of hydrate bound water found on $[Co(en)_3]Cl_3$ was variable and depended on the previous history of the sample. A sample of the complex was dried to the anhydrous condition in an oven at 150°C and after cooling and exposure to the atmosphere for 2–4 hr, the 2-hydrate was obtained; (Found; $H_2O$. 10·2 Calc. 9·45%) Apparently, the complex is very hygroscopic, with the composition approaching that of the 2-hydrate.

The anhydrous complexes began to decompose in the 170–270°C temperature range. The least stable was $[Co(NH_3)_4CO_3]NO_3$ and the most stable were $[Co(en)(C_2O_4)_2]$[Cl and $[Co(en)_2CO_3]Cl$. The thermal stability sequence, for complexes of the general formula, $[Co(amine)_2CO_3]Cl$, in order of decreasing stability, was: $[Co(en)_2CO_3]Cl > [Co(pn)_2CO_3]Cl > [Co(tn)_2CO_3]Cl$. The complex, $[Co(NH_3)_4CO_3]NO_3$, was even less stable thermally but this may be due to the presence of the nitrate ion in the ionization sphere. It should be pointed out that the thermal stability of the above complexes may be influenced more by the reaction of the compounds with air rather than the relative resistance to pyrolysis alone. The final product in the decomposition

of the complexes was $Co_3O_4$, or perhaps a mixture of $Co_3O_4$ and other cobalt oxides. Minimum temperatures for the oxide levels ranged from 600 to 685°C, with the exception of $[Co(NH_3)_4CO_3]NO_3$, which exploded at about 250°C, leaving a small residue of $Co_3O_4$ in the thermobalance pan. Stoicheiometric intermediate compounds, formed during the thermal decomposition process, were not found in the weight-loss curves.

*TGA Studies on metal oxalato complexes.* The TGA curves of the metal oxalato complexes, as determined by thermobalance II, are given in Fig. 3.

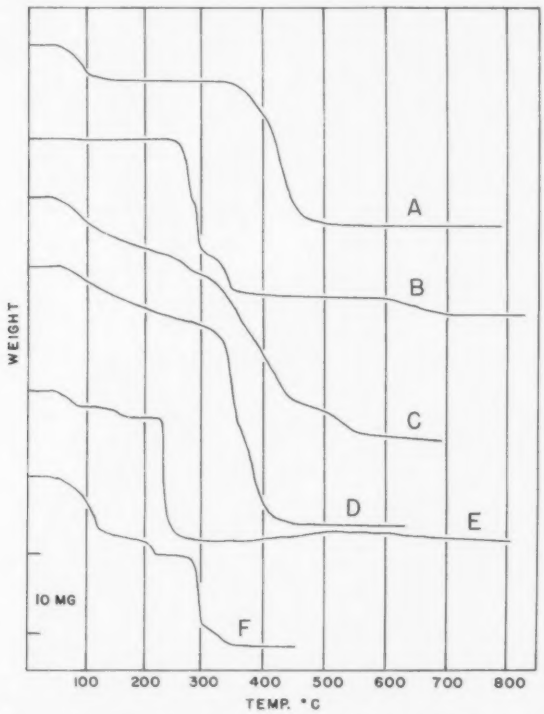


FIG. 3.—Thermal decomposition weight-loss curves of some metal oxalato complexes. Thermobalance II.
*A.* $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$; *B.* $K_3[Fe(C_2O_4)_3]$; *C. trans*-$K[Cr(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$; *D. cis*-$K[Cr(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$; *E.* $K_3[Rh(C_2O_4)_3]\cdot 2{\cdot}5H_2O$; *F.* $K_3[Co(C_2O_4)_3].4H_2O$.

In general, the water of hydration for the hydrate complexes began to come off in the 35–50°C temperature range. The anhydrous compounds, with the exception of *cis*- and *trans*-$K[Cr(C_2O_4)_2(H_2O)_2]$ hydrates, were formed in the 100–200°C temperature range. The complexes, *cis*- and *trans*-$K[Cr(C_2O_4)_2(H_2O)_2$ hydrates, did not yield anhydrous compounds after the loss of hydrate-bound water but began to gradually evolve co-ordinated water up to 250–350°C where the entire complex then began to decompose. The other anhydrous metal oxalato complexes were stable up to the 220–330°C temperature range. Further decomposition then took place to yield either metal oxide and potassium carbonate mixtures or, in the case of $K_2[Cr(C_2O_4)_3]\cdot 3H_2O$, $K_2CrO_4$ was the terminal decomposition product.

Several of the decomposition curves deserve comment. The *cis*- and *trans*-$K[Cr(C_2O_4)_2(H_2O)_2]$ hydrates complexes gave, as was expected, similar decomposition

curves. The only differences observed were above 400°C. The oxide (plus $K_2CO_3$) level was obtained at 450°C for the *cis*-salt while the *trans*-salt residue level was obtained at 575°C. The reason for this anomaly is not known since previous studies on another *cis*- and *trans*- series, $[Co(en)_2Cl_2]Cl$, yielded similar curves[4] after the water of hydration was evolved. Similar decomposition behaviour was noted for *cis*- and *trans*-$[Co(NH_3)_4Cl_2]Cl$, after the loss of hydrate-bound water on the *cis*-complex.[12] It is interesting to note that the co-ordinated water on the metal oxalato complexes began to come off before the hydrate-bound water was completely removed. A horizontal weight level was not observed for the anhydrous diaquated complex, $K[Cr(C_2O_4)_2(H_2O)_2]$, nor for the anhydrous complex, $K[Cr(C_2O_4)_2]$. Apparently, after the two co-ordinated waters are removed, the anhydrous complex is unstable and begins to decompose.

The rhodium (III) oxalato complex, as originally prepared, contained 4·5 waters of hydration. However, on standing in the laboratory preparatory to being studied on the thermobalance, it lost two waters of hydration so that the TGA curve is that for the complex, $K_3[Rh(C_2O_4)_3]\cdot 2\cdot 5H_2O$. Two of the hydrate-bound waters were evolved beginning at 45°C, giving a short horizontal weight level which corresponded approximately to $K_3[Rh(C_2O_4)_3]\cdot O\cdot 5H_2O$. This remaining water was then evolved beginning at about 110°C, to yield the anhydrous complex at 184°C. It has recently been shown by proton magnetic resonance studies that the rhodium complex has a half of mole of

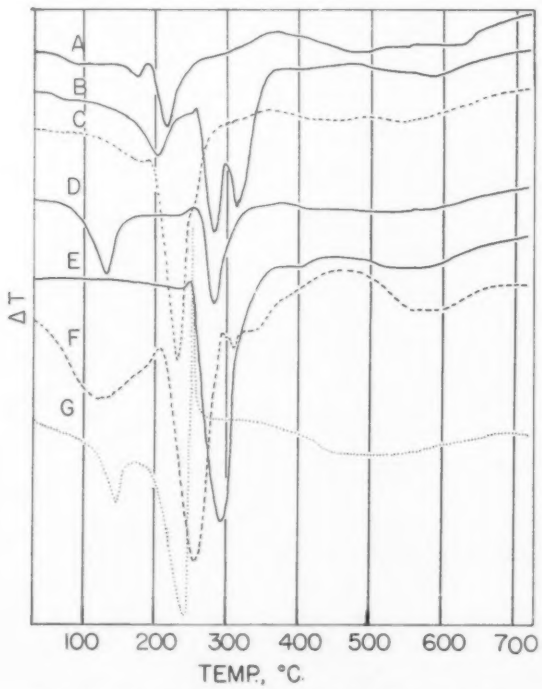


FIG. 4.—Differential thermal analysis curves of cobalt ammine complexes.
DTA apparatus I.
*A*. $[Co(tn)_3]Cl_3$; *B*. $[Co(en)(C_2O_4)_2]Cl\cdot H_2O$; *C*. $[Co(tn)_2CO_3]Cl\cdot H_2O$; *D*. $[Co(en)_3]Cl_3\cdot 2H_2O$;
*E*. $[Co(en)_2CO_3]Cl\cdot H_2O$; *F*. $[Co(pn)_2CO_3]Cl\cdot H_2O$; *G*. $[Co(NH_3)_4CO_3]NO_3\cdot H_2O$.

water bound in a somewhat different manner than the other four moles.[40] The TGA studies also confirm this viewpoint.

The TGA curve for $K_3[Co(C_2O_4)_3]$ revealed that it was a 4-hydrate instead of the normal 3-hydrate. The water of hydration began to come off at about 40°C, giving a break in the curve at 120°C. Further gradual weight-loss then took place, resulting in a horizontal weight level from 219 to 270°C, which did not correspond to the composition for the anhydrous compound, $K_3[Co(C_2O_4)_3]$. The residue weight-level was obtained at 360°C.

*DTA Studies on cobalt ammine complexes.* The DTA curves of the cobalt ammine complexes, as determined by DTA apparatus I, are given in Fig. 4.

All of the complexes, with the exception of $[Co(NH_3)_4CO_3]NO_3 \cdot H_2O$, gave only endothermic peaks below about 400°C, with broad exothermic peaks above this temperature. The dehydration endothermic peaks were quite evident for most of the hydrated complexes, occurring between room temperature and about 200°C. However, for $[Co(tn)_2CO_3]Cl \cdot H_2O$, the dehydration process was not completed before the complex itself began to decompose. This behaviour resulted in a broad dehydration peak which did not return to the base line before the appearance of the decomposition endothermic peaks. On the basis of peak maxima temperatures, the stability of the hydrates can be given as: $[Co(pn)_2CO_3]Cl \cdot H_2O < [Co(en)_3]Cl_3 \cdot 2H_2O < [Co(NH_3)_4CO_3]NO_3 \cdot H_2O < [Co(tn)_2CO_3]Cl \cdot H_2O < [Co(en)(C_2O_4)_2]Cl \cdot 2H_2O$.

The endothermic decomposition peaks were found in the 225–350°C temperature range. In all cases but one, a single decomposition peak was observed, with $[Co(en)(C_2O_4)_2]Cl \cdot H_2O$ giving a doublet. The behaviour of $[Co(NH_3)_4CO_3]NO_3 \cdot H_2O$ was different in that after a well defined, single endothermic peak, a sharp exothermic peak, with a peak maxima at 250°C, was observed. This latter peak was not unexpected in view of the explosive nature of this complex. In terms of thermal stability, as evaluated from the decomposition peak maxima temperatures, the complexes can be arranged in the sequence:

$$[Co(tn)_3]Cl_3 < [Co(tn)_2CO_3]Cl \cdot H_2O < [Co(NH_3)_4CO_3]NO_3 \cdot H_2O < [Co(pn)_2CO_3]Cl \cdot H_2O < [Co(en)_3]Cl_3 \cdot 2H_2O < [Co(en)(C_2O_4)_2]Cl \cdot H_2O < [Co(en)_2CO_3]Cl \cdot H_2O.$$

For the carbonato complexes, containing chloride ions in co-ordination sphere, this is the same thermal stability order as was found in the TGA study.

*DTA Studies on metal oxalato complexes.* The DTA curves of the metal oxalato complexes, as determined by DTA apparatus II, are given in Fig. 5.

In general, the complexes exhibited endothermic peak maxima, corresponding to dehydration reactions, in the 100–150°C temperature range. The dehydration peaks were rather sharp in the case of $K_3[Co(C_2O_4)_3] \cdot 4H_2O$ and $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$, but were very broad for the *cis*- and *trans*-$K[Cr(C_2O_4)_2(H_2O)_2]$ hydrates and the rhodium complex. The thermal stability order, based upon the dehydration peak maxima, was:

$$K_3[Cr(C_2O_4)_3] \cdot 3H_2O < K_3[Co(C_2O_4)_3] \cdot 3H_2O = \textit{trans}\text{-}K[Cr(C_2O_4)_2H_2O)_2] \cdot 3H_2O < \textit{cis}\text{-}K[Cr(C_2O_4)_2(H_2O)_2] \cdot 2H_2O = K_3[Rh(C_2O_4)_3] \cdot 2{\cdot}5H_2O.$$

The decomposition of the complexes gave a series of broad exothermic peaks in the

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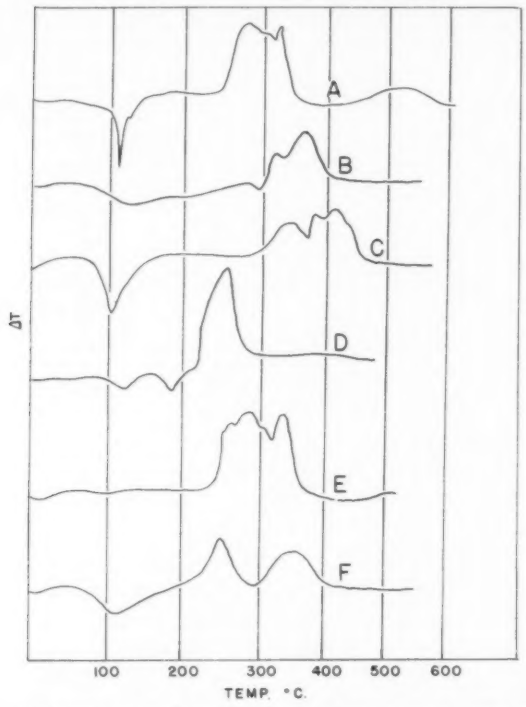


FIG. 5.—Differential thermal analysis curves of metal oxalato complexes.
DTA apparatus II.
*A*. $K_3[Co(C_2O_4)_3]\cdot 4H_2O$; *B*. *cis*-$K[Cr(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$; *C*. $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$;
*D*. $K_3[Rh(C_2O_4)_3]\cdot 2{\cdot}5H_2O$; *E*. $K_3[Fe(C_2O_4)_3]$; *F*. *trans*-$K[Cr(C_2O_4)_2(H_2O)_2\cdot 3H_2O$.

250–450°C temperature range. This behaviour was different from that observed for the cobalt ammine complexes in which mostly endothermic decomposition peaks were observed. There was a pronounced difference in the decomposition peaks for the *cis*- and *trans*-$K[Cr(C_2O_4)_2(H_2O)_2]$ hydrates. The *trans*- complex gave two broad exothermic peaks centered at 255° and 355°C, respectively, while the *cis*- complex gave a broad peak at 370°C containing a shoulder peak at 325°C. The explanation for this is not known although this behaviour might be expected judging from the results of the TGA curves.

*Acknowledgements*—We wish to express our thanks to Dr. C. BRICKER for supplying the $K_3[Fe(C_2O_4)_3]$, Dr. W. PLUMB for the $K_3[Rh(C_2O_4)_3]\cdot 4{\cdot}5H_2O$, Dr. G. LAPIDUS for supplying some of the cobalt carbonato complexes, and to Dr. G. M. HARRIS for stimulating discussions and his kind interest in this work.

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# THE INTERACTION OF $NO_2$–$N_2O_4$ AND CERTAIN METALLIC OXIDES: TERBIUM SESQUIOXIDE, LANTHANUM OXIDE, VANADIUM SESQUIOXIDE AND PEROVSKITE PHASE $PrCrO_3$*

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**Abstract**—The interaction of $NO_2$–$N_2O_4$ with terbium sesquioxide, lanthanum oxide, vanadium sesquioxide, and perovskite phase $PrCrO_3$ has been studied as a function of the temperature of interaction and the pressure of $NO_2$. Two methods of investigation have been employed: (a) analysis of the reacted species and (b) the infra-red spectra of the reacted products. It has been found that the interaction leads to oxidation, nitration and nitrition as competing processes.

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THE interaction of $NO_2$–$N_2O_4$ with terbium, lanthanum, and vanadium sesquioxides and perovskite phase $PrCrO_3$[1] has been investigated as part of a programme to elucidate the oxidation chemistry of metallic oxides in the presence of nitrogen dioxide. It is known that the interaction of $NO_2$ and metallic oxides may lead to the formation of the corresponding metallic nitrate,[2] or under the appropriate conditions $NO_2$ may act as an oxidizing agent as well as a nitriting agent.[3] It was felt to be of considerable interest to investigate the interaction of $NO_2$ and a series of oxides of differing basic and oxidative character. Terbium oxide exemplifies an oxide system with a wide range of metallic stoicheiometry and a relatively basic central metal ion. It is known that $TbO_{1\cdot5}$ may undergo oxidation and exist in a stoicheiometry range of $1\cdot5 < X < 2\cdot00$,[4–12] yet it is nearly as basic in character as magnesium oxide.[13,14] Lanthanum oxide represents the case of a relatively basic oxide system[13,14] with a comparatively stable stoicheiometry.[15] It may be anticipated that due to the more basic character of lanthanum oxide there will be a greater retention of nitrogen oxides with no apparent oxidation. It is of interest in this regard to distinguish the possible modes of interaction that can lead to the formation of the trinitrate;[2] i.e. the disproportionation of adsorbed $N_2O_4$ directly into $NO_3^-$, directly into $NO_2^-$ followed by

* This work was supported by the Massachusetts Institute of Technology under a contract from the Lincoln Laboratories; an organization under the joint support of the Army, Navy and Air Force.

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oxidation to $NO_3^-$, or the alternative of lattice oxidation followed by assimilation of nitrogen oxide to give $NO_3^-$ groups.

The study of a relatively non basic vanadium sesquioxide offers a contrasting example of a oxide system that can exist in the stoicheiometry range of $1{\cdot}5 < X < 2{\cdot}5$.[16,17,18] In addition to this a (II+) state also may exist but is not normally found in the solid state. The more common oxidation state is represented by the oxide composition $V_2O_5$ while $V_2O_3$ may be produced by the reduction of the higher oxide in dry hydrogen.[18] The reduced oxide is known to exist in the form of the corundum phase of alumina. Further, $V_2O_3$ exhibits very interesting semiconductive properties[19] which would indicate a structure in which a central vanadium ion has a strong energy exchange with its six metallic and four nonmetallic neighbours. Because of the lesser basic character of $V_2O_3$ it may be expected that nitration and nitrition will be a less prominent process than oxidation.

The study of $PrCrO_3$ offers the further alternative of an oxide system that is relatively stable to stoicheiometric changes. This seems to be the case for perovskite structures in general, for it appears that the structure is considerably stabilized by Jahn Teller forces. It may be anticipated that as a result of this inherent structural stability this material will resist changes in oxidation stoicheiometry as well as resist incorporation of nitrate, although both praseodymium and chromium oxides can be nitrated.[2]

## EXPERIMENTAL

The terbium oxide used in this study was obtained from the Lindsay Chemical Company and had a purity of 99·9 per cent. This material was obtained as the air ignited oxide, $Tb_4O_7$ which was subsequently reduced in dry hydrogen at 750°C. The residual hydrogen was then removed at 750°C until a pressure of $10^{-5}$ mm Hg was obtained. The sample was then quenched to room temperature. The cubic $-C$ configuration of the sesquioxide was obtained.[20,21]

The lanthanum oxide was also obtained from the Lindsay Chemical Company and was of a purity of better than 99·9 per cent. This material was ignited at 750°C under vacuum to remove adsorbed water and carbon dioxide and used without further treatment.

The vanadium oxide used in this study was obtained from the Baker Chemical Company and had a purity of about 99 per cent inclusive of water etc. The material was air oxidized below 600°C, to remove adsorbed water and carbon dioxide and to establish the (V+) stoicheiometry. It was weighed in this form and subsequently reduced to $V_2O_3$ in dry hydrogen at 550°C. Although this proved to be a slow reduction it was found from experience that if the reduction was initiated at this temperature and programmed to reach a higher temperature (750°C) the reduction could be completed within the cycling time of the system. On cooling, $V_2O_3$—corundum phase—was obtained.[19]

The $PrCrO_3$—perovskite phase—was prepared via a modification of the method of WOLD and WARD.[1] Stoicheiometric quantities of praseodymia, $Pr_6O_{11}$ and potassium chromate, $K_2CrO_4$ were carefully weighed to one part in $10^5$–$10^6$. The praseodymia was dissolved in nitric acid, and the potassium chromate in water. The chromate ion was reduced with acidified methanol. On completion of the rapid reduction the two solutions were combined and the metallic ions were precipitated with ammonium hydroxide. The hydroxide precipitate was dissolved in nitric acid and reprecipitated as before. In both cases, the completeness of precipitation was checked to a level of about $10^{-12}$ M for Pr and to about $10^{-20}$ M for Cr. The precipitate was ignited to 1000°C for 12 hr and 750°C for 32 hr. It was felt that this sintering procedure was adequate because the oxides were prepared from

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[21] A. IANDELLI, *Gazz. Chim. Ital.* **77**, 312 (1947).

the coprecipitated gelatinous hydroxides, thus producing a more finely divided oxide dispersion, which should hasten the sintering process and the formation of the perovskite material.

Since it was found that the composition of the $PrCrO_3$ varied with the temperature at which it had been air oxidized (see Fig. 11), it was felt that the reduced state would be a better representation for the standard state of stoicheiometry for $PrCrO_3$. Thus, the material was heated in about 5 cm Hg pressure of hydrogen at 750°C. In this way, it was possible to obtain a consistent oxidation state of $PrCrO_3$. It should be noted that further treatment in hydrogen did not alter the composition as evidenced by the consistency in the volume of hydrogen above the oxide. The consistency of the reduced state ($PrCrO_3$) may be partially justified in that praseodymia exhibits only metal deficient structures.[8,22] Although chromia generally exhibits similar nonstoicheiometric behaviour, it may also exhibit oxygen deficient stoicheiometry. In addition the stability of the perovskite phase would further lead one to believe that this material should have the composition $PrCrO_3$.

The nitrogen dioxide used in this study was obtained from the Matheson Chemical Company. This material was transferred from the storage tank to the vacuum line via a magnesium perchlorate drying trap, and was subsequently fractionated until the condensate was snow white.

The interaction between $NO_2$ and the metallic oxides was followed in a special vacuum line which was designed for this purpose. This system has been previously described.[3,23–26] Briefly the system consists of a storage system for $NO_2$, a reaction chamber,[3,23,26] an analytical system for the determination of oxides of nitrogen,[3] and pumping facilities.[24,25] The oxide under study was exposed for a specific period of time at a prescribed temperature and pressure. The excess of $NO_2$ was then removed by evacuation. The incorporated gases in excess of the stable phase, $TbO_{1.5}$, $LaO_{1.5}$, $VO_{1.5}$ and $PrCrO_3$, were then determined in the analytical system.

In addition to the analytical data, the infra-red spectra of the reacted products were also obtained. The reacted products were removed from the reaction chamber and mulled in Nujol. The spectra were obtained on a model 221 Perkin–Elmer double-beam spectrophotometer using sodium chloride optics.

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## RESULTS

### *Terbium oxide*

The interaction of $NO_2$–$N_2O_4$ and $TbO_{1.5}$ was studied as a function of the temperature of interaction between room temperature and 500°C and the pressure of $NO_2$ for a constant time of 17 hr. The interaction was found to involve a very sizable quantity (about 1–0·1 mole ratio) of physically adsorbed $NO_2$. In addition to the physically adsorbed $NO_2$ there was also a marked quantity of more tightly bound material. This nitrogenous material was removed by heating the sample to 750°C. The nitrogen content of the evolved gases was then determined volumetrically. Hydrogen was then admitted and the oxygen in excess of $TbO_{1.5}$, and the oxygen associated with the nitrogen was then determined. The results of the analysis are shown in Fig. 1, (a) and (b). The results are reported in $X$ stoicheiometric units of oxygen and $Y$ units of incorporated $NO_2$. With regard to Fig. 1(a), it may be seen that at a pressure of 26·5 cm Hg of nitrogen dioxide, the ratio $X$ reaches a maximum of 1·862 at 300°C. At a lower pressure of 0·014 cm Hg, a maximum of 1·60 is reached at a temperature of 300°C. At the same time the incorporated "$NO_2$" reaches a lesser maximum at 300°C for both pressures studied. As the temperature is decreased the $NO_2$ content rises quite markedly. It should be noted that for both pressures and all temperatures studied, the ratio $NO_2/O$, i.e. $Y/(X - 1{\cdot}5,)$ is always quite small (about 0·1) and thus the predominant process throughout is oxidation rather than nitration; for in the case of nitration the ratio would be one.

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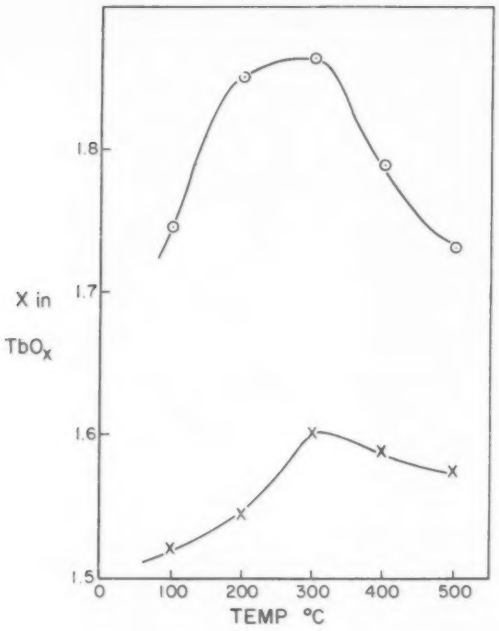
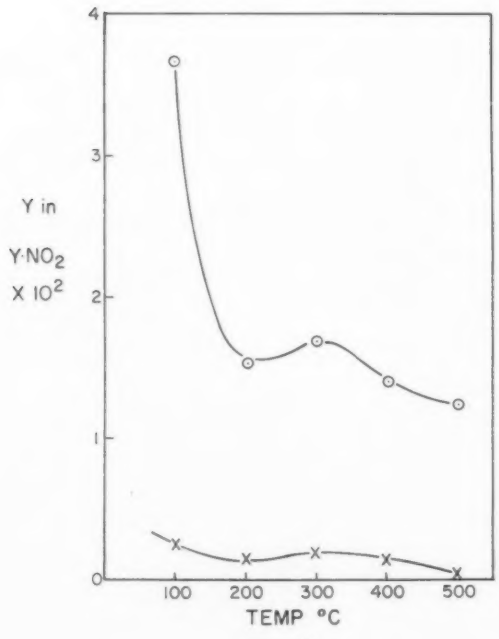



(a)




(b)

FIG. 1.—The stoicheiometry of the interaction of $NO_2$–$N_2O_4$ and $Tb_2O_3$ for (a) $X$ in $TbO_x$, (b) $Y$ in $YNO_2$ (O)$P_{NO_2} = 26{\cdot}5$ cm, ($X$)$P_{NO_2} = 0{\cdot}014$ cm, $t = 17$ hr.

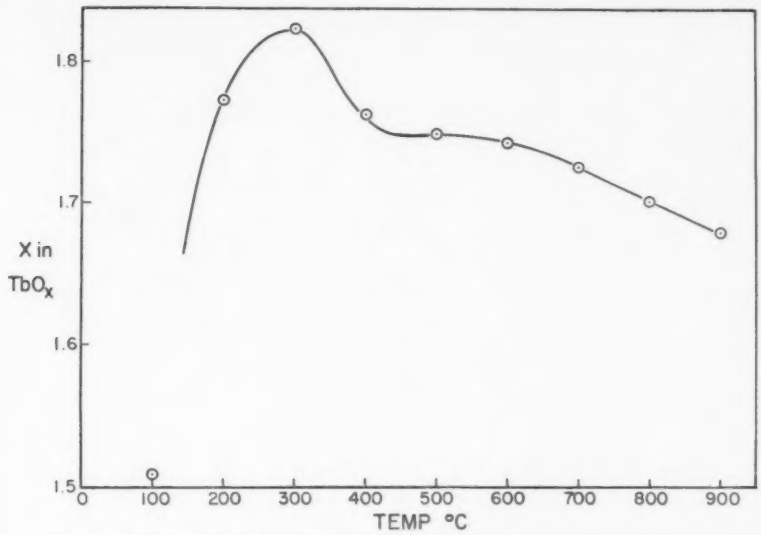



FIG. 2.—The stoicheiometry of oxidized terbia for $P_{O_2} = 76$ cm, $t = 17$ hr.

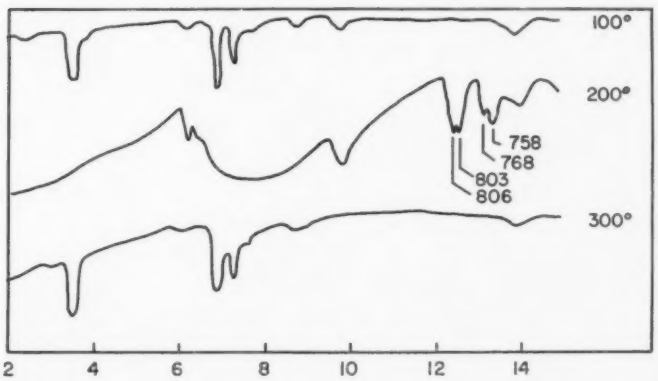



FIG. 3.—Spectra of the interaction product of $NO_2$–$N_2O_4$ and $Tb_2O_3$ for $P_{NO_2} = 26{\cdot}5$ cm, $t = 17$ hr at indicated temperatures. Ordinate: % transmission. Abscissa: microns.

As a comparison to oxidative interaction, the interaction of $TbO_{1{\cdot}5}$ and oxygen was studied as a function of the temperature of oxidation at $P_{O_2} = 76$ cm Hg. This is shown in Fig. 2. In this case the $X$ in $TbO_X$ rises to a maximum of 1·822 at 300°C, then declines with increasing temperature.

*Spectra and interpretation.* The infra-red spectra of the interaction products of $NO_2$ and $Tb_2O_3$ were obtained for samples maintained at various temperatures of interaction and at a pressure of 65·5 cm Hg of $NO_2$ (see Fig. 3). The period of interaction was 17 hr. The bands noted at about 3·5, 6·8 and 7·3 microns are due to uncompensated Nujol. Other bands may be noted at about 7·5, 8·6, 9·6, 12·35, 12·5, 13·0, 13·2 and 13·9 $\mu$. Of these, the band at about 8·6 $\mu$ is due to a metal bridged nitrite structure[3,27] while the bands at about 7·5 and 12·35 $\mu$ are due to ionic nitrate

[27] F. VRATNY, M. TSAI and F. GUGLIOTTA, *Nature, Lond.* **188,** 484 (1960).



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structure.[3,28] It is evident from the spectral data that the predominant structure at 100 and 300°C is nitrite, while the nitrate ion is quite in evidence at 200°C. Further, at 100 and 300°C there is a rather nominal amount of incorporated nitrogen while at 200°C a significant amount of nitrogen incorporation has occurred.

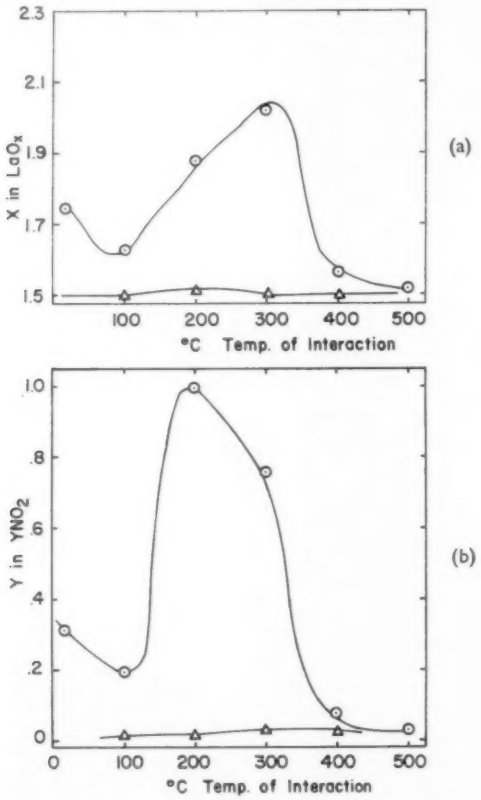


FIG. 4.—Stoicheiometry of the interacted product as a function of the temperature of interaction for $P_{NO_2} = 26{\cdot}5$ cm (O) and 0·014 cm (△). (a) $X$ in $LaO_X$ (b) $Y$ in $YNO_2$.

In this regard it should be noted that for the lower temperature (100°C) it is probable that the activation energy barrier toward nitration has not been exceeded and thus the chemisorbed layer is incorporated as nitrite. As the temperature is increased it is possible to accomplish the auto oxidation of nitrite to nitrate, while at still higher temperatures (300°C and up) the interacted phase becomes thermally unstable with respect to nitrate and thus may incorporate only nitrite. In all cases it should be noted that the nitrogen incorporation reaction is only about 10 per cent of the oxidation reaction which tends to establish a stable equilibrium at known stable phases of $TbO_X$.[29]

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[29] W. D. KINGERY (Editor). *Kinetics of High Temperature Processes*. Wiley, New York (1959).

*Lanthanum oxide*

The interaction of $NO_2$–$N_2O_4$ and $LaO_{1\cdot5}$ was studied as a function of the temperature of interaction between room temperature and 500°C and the pressure of $NO_2$ for a constant period of interaction of 17 hr. The interaction was found to lead to a large uptake (about 0·1–3·0 mole ratio) of physically adsorbed $NO_2$. This material was rapidly removed by evacuation of the sample preceding analysis. In addition to this, an

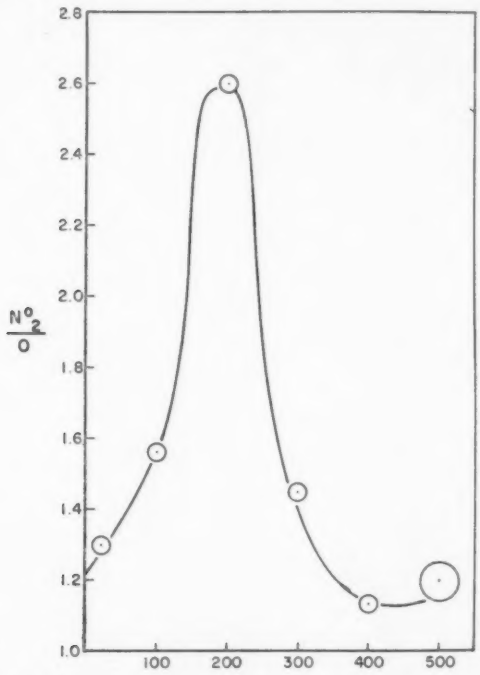



FIG. 5.—$NO_2/O$ as a function of the temperature of interaction for $La_2O_3$. Ordinate: $NO_2/O$. Abscissa: temperature of interaction.

uptake of more tightly adsorbed nitrogen oxides was noted. This material was removed by heating the reacted material at 750°C and then treated as in the above case of terbia.

Due to the fact that it was impossible in this determination to distinguish the forms of incorporated nitrogen, i.e. $NO_2$, $NO_2^-$, $NO_3^-$, the data is reported as $X$ stoicheiometric units in $LaO_X$, $Y$ stoicheiometric units in $Y\ NO_2$. It is evident that if $X = Y$, one can infer the presence of the nitrate radical. It may be noted in Fig. 4, that for a pressure of 26·6 cm Hg of $NO_2$, both the $X$ and $Y$ ratios decrease as a function of temperature from room temperature to about 100°C, then rise rapidly to a maximum at about 200°C, and then decrease again at higher temperatures.

At a pressure of 0·014 cm Hg, there is a significant excess of oxide in excess of nitrogen dioxide only in the range of 200°C, where an increase in the $X$ ratio is evident. This would indicate the existence of $NO_3^-$ in this range. It may be noted in Fig. 5 that the ratio $NO_2/O$, i.e. $Y/(X - 1\cdot5)$ is always larger than one and that a maximum is reached at about 200°C. For the lower pressure mode of interaction, the ratio is always larger than one. In most cases, the ratio is much larger than one. This

suggests, that although nitrate may be present, it is only a preferred specie at higher pressures of $NO_2$. There is in all cases also a significant amount of incorporated "$NO_2$".

*Spectra and interpretation.* The infra-red spectra of the interaction products of $NO_2$ and $LaO_{1\cdot5}$ were obtained for samples reacted at various temperatures and a pressure of 26·6 and 0·014 cm Hg of $NO_2$ for 17 hr interaction time (see Figs. 6 and 7).

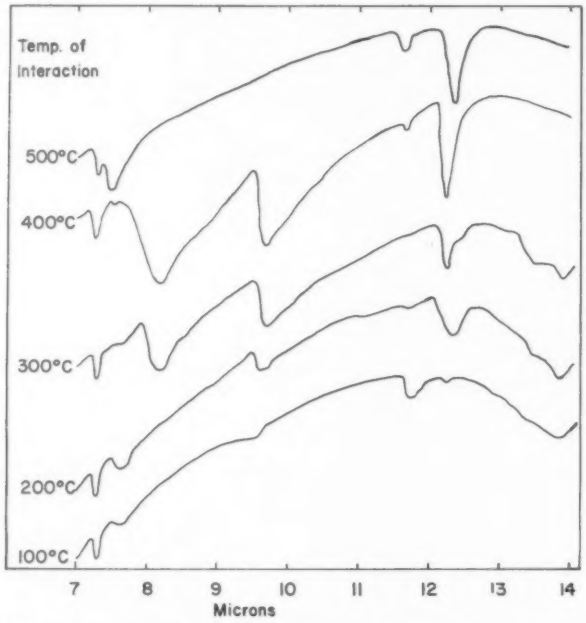
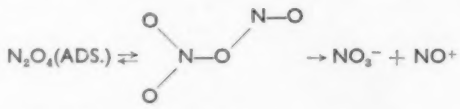



FIG. 6.—Infra-red spectra of the interaction products of $NO_2$–$N_2O_4$ and $La_2O_3$ for various temperatures of interaction at $P_{NO_2} = 26{\cdot}5$ cm and 17 hr. Abscissa: microns. Ordinate: % transmission.

The band noted at 7·3 $\mu$ is due to uncompensated Nujol. Other bands are to be noted at about 7·6, 8·15, 9·8, 11·7 and 12·2 $\mu$. The bands at 7·6, 9·6 and 12·2 $\mu$ are due to ionic nitrate,[28] while the band at 8·15 $\mu$ is due to metallic nitrite.[27,30]

It may be seen in Figs. 6 and 7 that metallic nitrate is present at all temperatures of interaction while the presence of metallic nitrite is apparent only in the temperature range of 200–400°C. In conjunction with the analytical data it may be inferred that while nitration is a prominent process in the interaction, the process of nitrition is also a prominently competing process—particularly at lower pressures of $NO_2$. The above would seem to suggest a mode of interaction initiated by a physically adsorbed layer of $NO_2$–$N_2O_4$ which is followed by chemisorption. In the form of adsorbed $N_2O_4$ it may be possible that we may have nitrate ion production via the PAULING resonance structure:[31,32]




[30] D. WILLIAMS, *J. Amer. Chem. Soc.* **61**, 2987 (1939).
[31] L. PAULING, *Nature of the Chemical Bond* (2nd Ed.). Cornell University Press, Ithaca, N.Y. (1948).
[32] P. GRAY and A. D. YOFFE, *Quart. Rev.* **9**, 385 (1955).

A possible alternative is the production of the nitrate ion via adsorbed $NO_2$ and lattice oxide ion:

$$NO_2(ADS.) + O^{2-} \rightarrow NO_3^- + (\square^-)$$

with the production of a negative defect. A number of consumption steps are possible

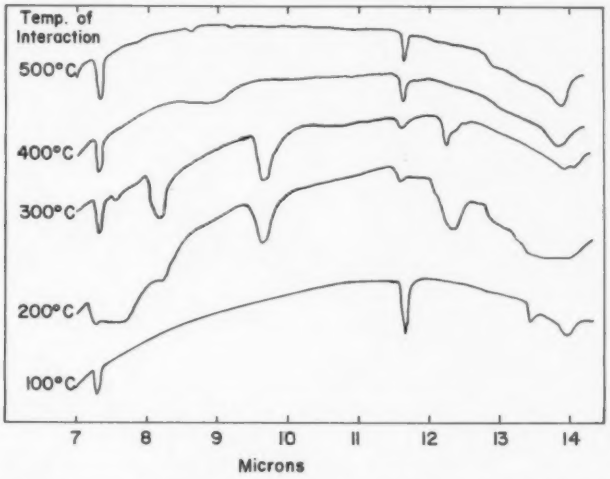



FIG. 7.—Infra-red spectra of the interaction products of $NO_2$–$N_2O_4$ and $La_2O_3$ for various temperatures of interaction at $P_{NO_2} = 0{\cdot}014$ cm and 17 hr. Ordinate: % transmission. Abscissa: microns.

of which three are listed to indicate the possible origin of $NO_2^-$ and NO found in the above interaction:

$$NO_2(ADS.) + (\square^-) \rightarrow NO_2^-$$

$$NO_2^- \rightarrow NO + O^- + (\square^+)$$

$$NO_2^- + NO_2(ADS.) \rightarrow NO + NO_3^-.$$

*Vanadium sesquioxide*

The interaction of $NO_2$–$N_2O_4$ and $VO_{1{\cdot}5}$ was studied as a function of the temperature of interaction between room temperature and 500°C and the pressure of $NO_2$ for a constant time of 17 hr. The interaction was found to involve a sizable quantity of physically adsorbed $NO_2$. (0·1–1·0 mole.) This loosely bound adsorbate was removed during the evacuation step while the more tightly bound material was determined in the analytical system as in the preceding cases. The results are shown in Figs. 8(a) and (b), and are reported in $X$ stoicheiometric units of oxygen in $VO_X$ and $Y$ units of $NO_2$ in $Y$ $NO_2$.

For both pressures of $NO_2$ studied, the oxygen content increased with increasing temperature of interaction. The $NO_2$ content however decreased with increasing temperature at a pressure of 26·5 cm Hg of $NO_2$, and was nearly constant at the lower pressure of interaction (0·014 cm Hg). Further, the ratio of oxidation to incorporation of $NO_2$ is of the order of $10^3$ at 26·6 cm Hg and $10^4$ at a pressure of 0·014 cm Hg. It is

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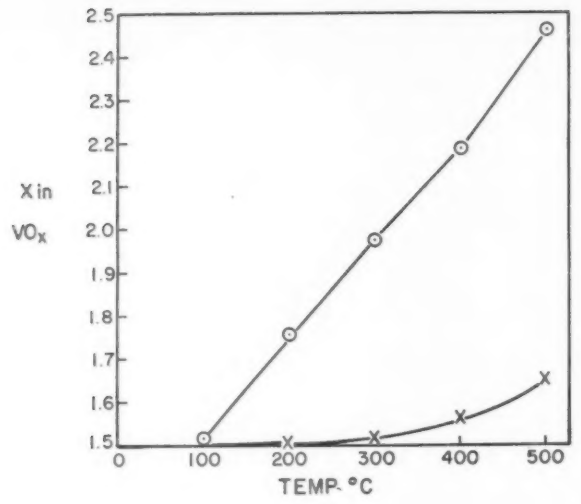
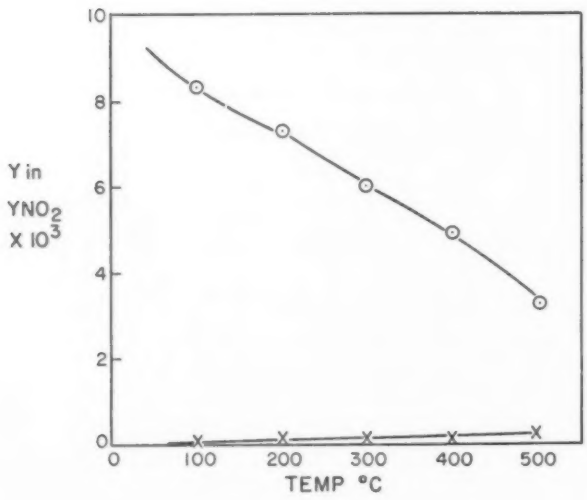



(a)




(b)

FIG. 8.—The stoicheiometry of the interaction products of $NO_2$–$N_2O_4$ and $VO_{1\cdot5}$ at various temperatures of interaction for 17 hr $P_{NO_2}$ = 26 5 cm Hg (O), 0 014 cm Hg (*X*), (a) *X* in $VO_X$, (b) *Y* in $YNO_2$.

evident that the oxidation process in this instance is greatly in precedence to that of the incorporation of nitrogen dioxide.

As a comparative study, the oxidation of $VO_{1\cdot5}$ was investigated at a $P_{O_2}$ = 76 cmHg for a period of 17 hr. Generally, it was found that the oxidation did not proceed as far as the corresponding $NO_2$ oxidation at a pressure of 26·6 cm Hg. Below 200°C the oxidation seemed nearly insignificant and only in the 500°C range did the reaction proceed to the $VO_{2\cdot5}$ state, although $VO_2$ is approached in the 350°C region.

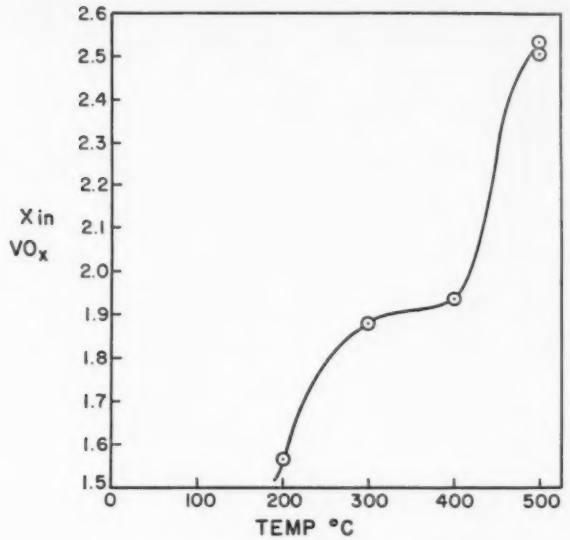



FIG. 9.—The stoicheiometry in the oxidation of $VO_{1\cdot5}$ at various temperatures for 17 hr at a $P_{O_2} = 76$ cm Hg.

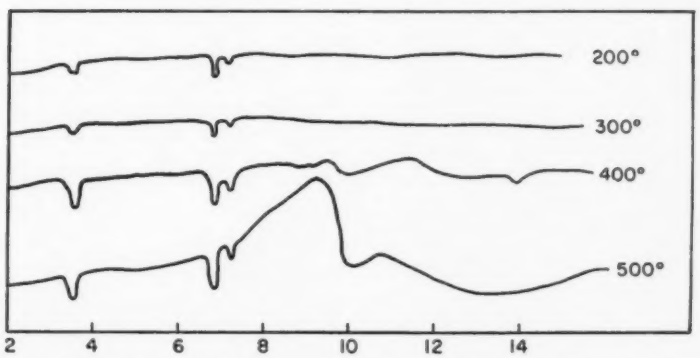



FIG. 10.—The spectra of the interaction products of $NO_2$–$N_2O_4$ and $VO_{1\cdot5}$ at various temperatures for 17 hr. $P_{NO_2} = 65\cdot5$ cm Hg. Ordinate: % transmission. Abscissa: microns.

*Spectra and interpretation.* The infra-red spectra of the interacted products were obtained for samples reacted at various temperatures and at a pressure of 65·5 cm Hg of $NO_2$ for 17 hr (see Fig. 10). The bands noted at about 3·5, 6·8 and 7·3 $\mu$ are due to the presence of uncompensated Nujol. No incorporated nitrogen could be detected. One would then conjecture that neither nitrate nor nitrite are present in the interaction. It should be noted that it is easily possible to detect these species at an oxygen to $NO_2$ ratio of $10^2$ and thus would be expected to be observable at the present level of $10^3$.[3,33]

Although it was not possible to observe the presence of incorporated nitrogen, it should be noted that the spectra of the samples reacted at 400–500°C show absorption bands in the 10–14 $\mu$ region. This is due to the V–O stretching vibration at 9·8 and

[33] F. VRATNY, *Nature, Lond.* **189,** 479 (1961).

12·1 $\mu$.[34,35] It may be noted that these bands do not occur in the spectra of the $VO_{1\cdot5}$ samples. This would suggest the lack of simple molecular bonding in $VO_{1\cdot5}$.

In conclusion, it is evident that the interaction of $NO_2$ and $VO_{1\cdot5}$ results in a predominant reaction of oxidation. This is accompanied by a much lesser reaction of physical adsorption of $NO_2$.

$PrCrO_3$

The air oxidation ($P_{O_2}$ = 14 cm Hg) of $PrCrO_3$ was studied as a function of the temperature of oxidation for periods of 17 hr. The composition of the oxide increased with the temperature of oxidation and reached a maximum at about 500°C, followed

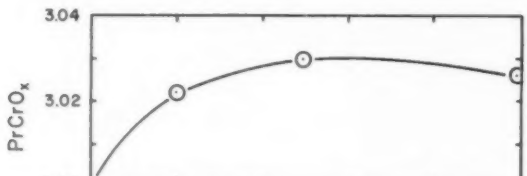



FIG. 11.—An oxidation ($P_{O_2}$ = 14 cm Hg) of $PrCrO_3$ for 17 hr as a function of temperature. $X$ in $PrCrO_X$ is plotted as a function of temperature of oxidation.

by a slight decrease in the oxidation stoicheiometry (see Fig. 11). These reported stoicheiometry units are valid to about 0·002, relative to the amount of material used.

The interaction of $NO_2$–$N_2O_4$ and $PrCrO_3$ was studied as a function of the temperature of interaction and the pressure of $NO_2$. A constant period of interaction was used throughout—17 hr. During the interaction there was a sizable uptake (0·1–1·0 mole quantity) of physically adsorbed $NO_2$. This was rapidly removed by evacuation and was not further considered. In addition, a certain amount of nitrogen was more strongly retained. This incorporated nitrogen was driven off at 750°C and the sample treated as in the preceding cases. The data in Figs. 12(a) and (b) are presented as $PrCrO_X \cdot XNO_2$, where the $X$'s represent units of stoicheiometry.

It may be seen in Fig. 12 that as the pressures of $NO_2$ increase, the oxidation and incorporation of $NO_2$ in $PrCrO_3$ increase. Further, at any given pressure of $NO_2$ the two quantities ($NO_2$ and O) reach a maximum at a temperature of about 100°C, then tend to gradually decrease. The results are further illustrated by obtaining the ratio of incorporated $NO_2$ to oxygen excess. This may be represented as: $NO_2/O$ or ($X$ in $XNO_2/X$ in $PrCrO_X - 3$) plotted as a function of the temperature of interaction (see Fig. 13). With this type of presentation a ratio of one indicates the presence of $NO_3^-$. A ratio of less than one indicates oxidation in addition to other nitrogen incorporation reactions. For a pressure of 65·5 cm Hg of nitrogen dioxide the ratio is nearly constant with a value of one. For the lower pressure of nitrogen dioxide the ratio is always smaller than one.

*Spectra and interpretation.* The infra-red spectra were obtained for samples interacted for 17 hr at a pressure of 65·5 cm Hg of nitrogen dioxide. Representative spectra

[34] G. G. BARRACLOUGH, J. LEWIS and R. S. NYHOLM, *J. Chem. Soc.* 3552 (1959).
[35] F. VRATNY, M. DILLING, C. N. R. RAO and F. GUGLIOTTA. To be published.

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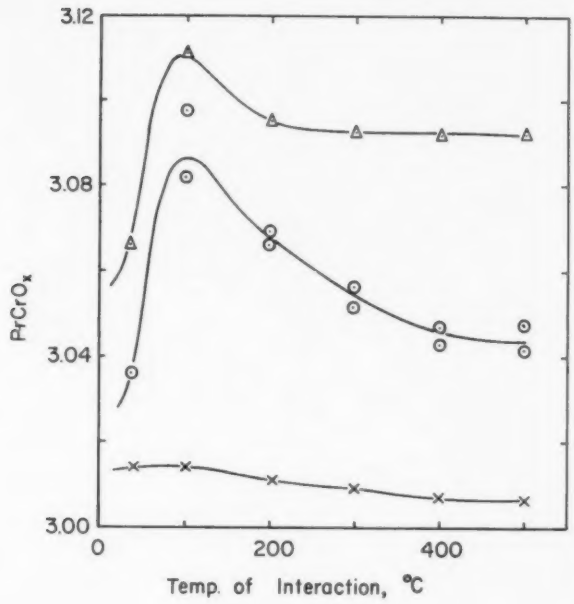
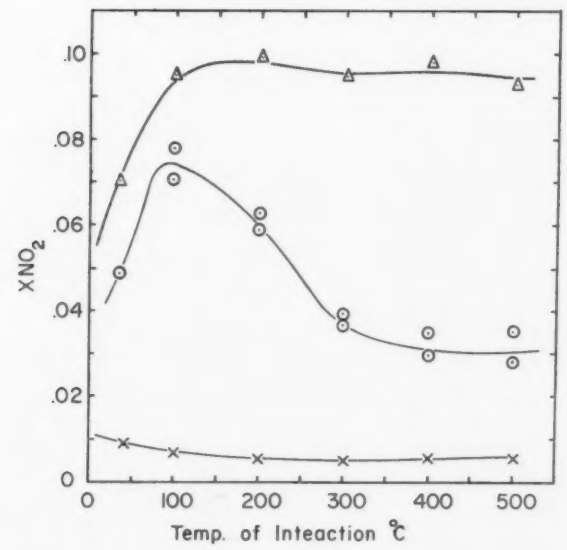



(a)




(b)

FIG. 12.—(a) Oxygen in excess of $PrCrO_3$ and $NO_2$ ($X$ in $PrCrO_X$). (b) Incorporated $NO_2$ ($X$ in $XNO_2$) as a function of the temperature of interaction at three pressures of $NO_2$: (△) 65·5 cm Hg, (O) 26·5 cm Hg, ($X$) 0·014 cm Hg.

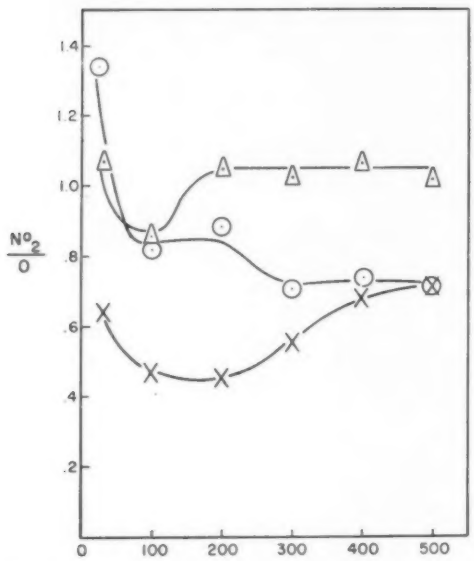



FIG. 13.—The ratio $NO_2/O$ as a function of the temperature of interaction for three pressures of $NO_2$ for $PrCrO_3$: (△) 65·5, (⊙) 26·5, (×) 0·014 cm Hg.

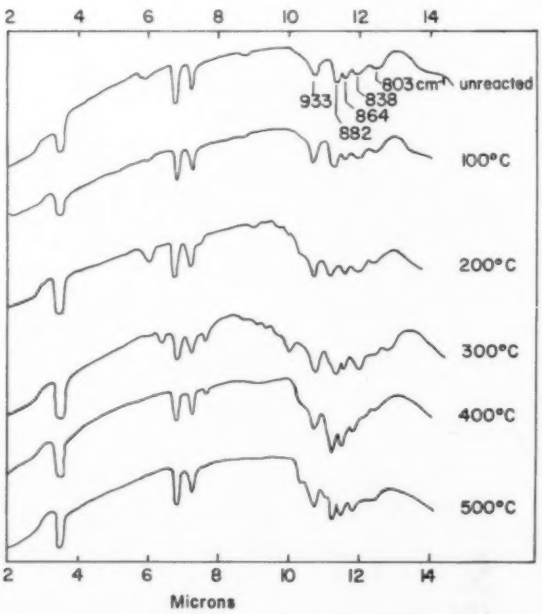



FIG. 14.—Spectra of interaction product $NO_2$–$N_2O_4$ and $PrCrO_3$ at $P_{NO_2} = 65·5$ cm Hg for 17 hr. Ordinate: % transmission. Abscissa: microns.

are reproduced in Fig. 14. The top spectrum represents unreacted $PrCrO_3$. The bands noted at about 3·5, 6·8 and 7·2 $\mu$ are due to the presence of uncompensated Nujol. The bands in the 10–12 $\mu$ region are characteristic of chromium–perovskite compounds.[35] The remaining spectra are representative of the interaction products obtained at the indicated temperatures of interaction.

In addition to those mentioned above, two bands are to be noted at about 7·5 and 12·0 $\mu$. The band at 12·0 $\mu$ overlaps a similarly located band due to $PrCrO_3$. It may be noted that the intensity of this band gradually increases and reaches a maximum at a temperature of about 300°C, then decreases at higher temperatures of interaction. The band at about 7·5 $\mu$ is first noted as a shoulder on the Nujol band in the spectrum for the sample reacted at 200°C. The band shows an increase in intensity for the next temperature—300°C, followed by a decrease on intensity at higher temperatures. These two bands are directly correlated with ionic nitrate.[28]

From the spectral data it may be seen that at high pressures of $NO_2$ the nitrate ion can exist as a discrete structural unit. From the analytical data there is a strong indication of nitration at a pressure of 26·5 cm Hg of $NO_2$. It would thus seem evident that interaction of $NO_2$ and $PrCrO_3$ leads directly to the formation of the nitrate ion. However, the analytical data would further indicate that oxidation is a coexisting process for the lower pressure of $NO_2$. This is particularly the case at elevated temperatures as evidenced in Figs. 12 and 13.

It is felt that this type of interaction arises from the characteristics of the perovskite oxide oxidation stoicheiometry and does not occur as a result of deviations in metal ion stoicheiometry.

*Acknowledgements*—The author wishes to thank Mrs. M. DILLING for her assistance in taking some of the spectra and Mr. F. GUGLIOTTA for his assistance in taking some of the data.

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# THE REACTION OF $PuF_4$ WITH OXYGEN

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(*Received* 6 *December* 1960)

**Abstract**—The reaction of $PuF_4$ with dry oxygen has been studied between 750–900°C. There was some evidence for the production of $PuF_6$, but if this is in fact formed, the rate of reaction is several orders of magnitude slower than that of the corresponding reaction of $UF_4$ with oxygen. $PuF_4$ does, however, appear to be volatile in a stream of oxygen at these temperatures. No trace of plutonium oxide was found in the residue.

IT had been shown[1] that plutonium trifluoride is completely volatile in a mixture of oxygen and HF at 800°C, and that, above this temperature, the hydrofluorination in the presence of oxygen of the dioxide, the tetroxalate or the tetrafluoride leads to a complete volatilization of the starting material. This suggested that $PuF_6$ might be obtained by the action of $O_2$ on $PuF_4$ in an analogous manner to the preparation of $UF_6$ described in the preceding paper.

## EXPERIMENTAL

The procedure was similar to that used for the $UF_4/O_2$ reaction (see preceding paper). The apparatus was enclosed in a double-skinned glove-box because of the health hazard involved in handling volatile plutonium compounds, and this precaution increased the difficulty of manipulation. When the reaction was complete the break-seal tube was sealed off and, after inspection, the break-seal was broken under dilute nitric acid. The tube was then cracked open and well washed. The resulting solution was analysed by α-counting for plutonium and by pyrohydrolysis for fluorine.

The $PuF_4$ was prepared by the hydrofluorination of Pu(IV) oxalate at 550°C and X-ray diffraction photographs did not show any phase other than $PuF_4$ to be present.

The results are shown in Table 1.

## DISCUSSION

(i) Above 800°C, plutonium tetrafluoride is volatile in a stream of dry oxygen.

(ii) When the oxygen is moist, $PuO_2$ is formed at 750°C, and the reaction, used in the analysis of plutonium fluorides by pyrohydrolysis, appears to occur:

$$PuF_4 + 2H_2O \rightarrow PuO_2 + 4HF \qquad (1)$$

However, when the oxygen is dry, there appears to be some reaction which results in the production of a volatile plutonium compound. In run D4 (27 hr at 850°C) for instance, 15 mg of plutonium were found in the break-seal, and in other runs smaller quantities of plutonium were detected. The break-seal being at a "dead-end" of the apparatus it is hard to see how the element could have been carried into it as dust, and it seems certain that any material found therein must have undergone sublimation *in vacuo* at room temperature.

(iii) There is evidently a difference in the course of the reaction between $PuF_4$ and $O_2$, and $UF_4$ and $O_2$. FLORIN[3] and the present authors with others[4] have pointed

* Present address: Ruloe House, Cuddington, Northwich.

[1] J. K. DAWSON and A. E. TRUSWELL. Unpublished work, A.E.R.E., Harwell (1951).

TABLE 1.

| Run | Weight of $PuF_4$ (mg) | Temp. (°C) | Time (hr) | Weight of residue (mg) | X-Ray evidence | Comments on residue | Pu in break-seal (mg) | Comments on sublimate | General comments |
|---|---|---|---|---|---|---|---|---|---|
| D2 | 390 | 900 | 4½ | 384 (including sublimate) | $PuF_4$ only | Considerable sublimation from the boat. Weight of residue includes flakes scraped from reaction tube | None | — | No volatile product? Total sublimation before reaction could take place |
| D3 | 1190 | 850 | 4 | 1094 | — | This amount of residue (dark brown) remained in the boat, some sublimate was firmly adherent to the reaction tube | Trace | Much white sublimate ($?SiF_4$) in the break seal | — |
| D4 | 1423 | 850 | 27 | 977 | — | This boat was empty except for a few black stains. Much dark-red-brown sublimate on furnace walls. Traces of attack on silica U-tube with formation of a white or yellowish compound | 15 | 0·5 ml of white sublimate. Sublimed into side arm: m.p. ca. 200°K (m.p. $SiF_4$ 196°K) contained 33 mg F, i.e. a fourfold excess over the calculated quantity if all the plutonium was present as $PuF_6$ | The white sublimate turned violet below 200°K and a bright pink at liquid oxygen temperatures; these colour changes were reversible |
| D5 | 1829 | 850 | 27½ | — | — | As D4 | 3 | White sublimate as $D_4$ | as $D_4$ |
| D1 | 585 | 800 | 4 | 569 | $PuF_4$ only | — | 1 | — | — |
| D6 | 240 | 750 | 4¼ | Nil in boat from walls | $PuF_4$ + $PuO_2$ | Two small flakes scraped from furnace walls | 0·023 | Some etching of break-seal | Much condensed water found in trap in which oxygen had been condensed. Oxygen presumed not dry, and hydrolysis had taken place. Run repeated |
| D7 | 235 | 750 | 4½ | 230 | $PuF_4$ only | Dark brown powder | None | — | 0·10 mg Pu found in washings from the U-tube |
| D8 | 180 | 750 | 5 | 170 | $PuF_4$ only | Dark brown powder | Trace | — | — |
| — | — | 600 | DAWSON *et al.*[2] found no reaction at 600°C or at lower temperature | | | | | | |

[2] J. K. DAWSON, R. M. ELLIOTT, A. E. TRUSWELL and R. HURST, *J. Chem. Soc.* 558 (1954).

out that in the reaction of $PuF_4$ with fluorine the rate is at least an order of magnitude slower than that in the similar reaction between $UF_4$ and $F_2$; even so, since the reaction of 1 g of $UF_4$ with oxygen at 900°C is complete in 2–3 min, if the $PuF_4 \xrightarrow{O_2} PuF_6$ reaction proceeded at an appreciable rate, it would be expected that there would be a reasonable yield of product after a run lasting for 27 hr. Only in one case was as much as 15 mg of plutonium found in the break-seal; this was approximately a 3 per cent yield on the assumption of a basic reaction:

$$2PuF_4 \xrightarrow{O_2} PuF_6 + PuO_2F_2 \qquad (2)$$

The fall in the rate of the reaction might be due to a reduction of the surface area due to slagging of the solid reactant, but reaction was inappreciable in the runs carried out at the highest temperature at which slagging did not take place (750°C).

Some reaction must, however, be occurring to account for (a) the disappearance of plutonium tetrafluoride from the reaction boat at temperatures at which the vapour pressure of $PuF_4$ is very low, and (b) the production of considerable quantities of $SiF_4$. The reactions

$$PuF_4 + 2H_2O \xrightarrow{O_2} PuO_2 + 4HF \qquad (3a)$$

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O \qquad (3b)$$

involving water-vapour are presumed to have occurred in run D6, where it was shown that moisture was present in the oxygen, and $PuO_2$ was detected in the X-ray diffraction photograph of the residue. Lines due to $PuO_2$ were not detected in the X-ray diffraction photographs of the residues from the other runs, although these lines are always well defined and easily distinguished from the much weaker ones due to $PuF_4$ observed in a mixture of both compounds. It is known that pyrohydrolysis of $PuF_4$ is rapid at 750°C, so that the absence of $PuO_2$ is good evidence both for the absence of moisture in the oxygen stream, and for the presumption that hydrogen fluoride and $SiF_4$ could not have been produced by reactions (3a) and (3b).

(iv) There remains the possibility that the reaction

$$2PuF_4 + O_2 \rightarrow PuO_2F_2 + PuF_6 \qquad (4)$$

occurred at least to some extent, for the $PuO_2F_2$ formed would be difficult to detect by X-ray diffraction analysis if its properties are similar to those of $UO_2F_2$. The latter is so hygroscopic that a few minutes exposure to atmospheric air obliterates its characteristic lines.

Since after run D7 an appreciable quantity of plutonium was found in the break-seal tube it is very probable that this had been conveyed there as volatile $PuF_6$, but there was no positive evidence for the formation of this compound. It can be stated that if such a reaction does take place, it proceeds much less readily than the corresponding reaction with $UF_4$, and that it is unsuitable for the preparation of $PuF_6$. The formation of this compound by the action of fluorine on $PuF_4$ has been described by the present authors with others (*loc. cit.*) and by WEINSTOCK *et al.*[5]

[3] A. E. FLORIN, J. R. TANNENBAUM and J. F. LEMONS, *J. Inorg. Nucl. Chem.* **2**, 368 (1956).
[4] C. J. MANDLEBERG, H. K. RAE, R. HURST, G. LONG, D. DAVIES and K. E. FRANCIS, *J. Inorg. Nucl. Chem.* **2**, 358 (1956).
[5] B. WEINSTOCK and J. G. MALM, *J. Inorg. Nucl. Chem.* **2**, 380 (1956).

## CONCLUSION

There is insufficient evidence to allow the action of oxygen on $PuF_4$ to be described. More information about the properties of $PuF_6$, $PuO_2F_2$ and $PuF_5$ are essential. The information on the action of fluorine on $PuF_4$ published elsewhere, does not throw any light on the course of the reaction described here.

*Acknowledgements*—We are indebted to Mr. E. FURBY who did the pyro-analyses for fluorine and to Professor P. L. ROBINSON for his advice in preparing this paper. We should like to express our thanks to the Director, A.E.R.E., Harwell, for his permission to publish this paper.

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# THE SOLVENT EXTRACTION OF PLUTONIUM AND AMERICIUM BY TRI-*n*-OCTYLPHOSPHINE OXIDE

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THE increasing use of organophosphorus compounds (such as TOPO, tri-*n*-octylphosphine oxide) in solvent extraction is due to their selectivity and efficiency in removing metal ions from aqueous solutions. TOPO dissolved in an inert hydrocarbon solvent is outstanding amongst the newer reagents. ROSS and WHITE[1] studied the extraction of several metal ions by TOPO, and published a preliminary qualitative survey. Later quantitative results,[2] and a detailed study of the extraction of thorium,[3,4] iron,[5] zirconium,[6] chromium,[7] and technetium[8] confirmed its effectiveness and new analytical methods for chromium,[9] titanium,[10] uranium,[11] zirconium[12] and thorium[13] involve a TOPO solvent-extraction stage.

Although TOPO will extract at least twenty-three different metal ions, the conditions for extraction vary considerably. Normally extraction is from acidic solutions, when the nature and strength of the acid are critical factors, e.g. TOPO extracts ferric iron from hydrochloric acid solutions but not from nitric, sulphuric, perchloric or phosphoric acid solutions. The charge on the metal ion is another critical factor; TOPO extracts ferric but not ferrous iron from hydrochloric acid, and hexavalent (i.e. chromate) but not di- or tri-valent chromium. In addition, a single extraction with TOPO under optimum conditions gives a quantitative separation.

The versatility outlined above indicated that TOPO might be of use in the separation of plutonium from other metal ions. This paper describes the extraction of plutonium in three valency states (III, IV, and VI) from nitric and hydrochloric acids of various strengths, and the properties of the plutonium (IV and VI)–TOPO complexes extracted into the organic phase from nitric acid. The extraction of americium (III) from nitric acid is also described.

## EXPERIMENTAL

### *Preparation of* 0·1 M-TOPO *in cyclohexane*

In the first experiments TOPO was prepared by the reaction of phosphorus oxychloride with the

[1] W. J. ROSS and J. C. WHITE, Report ORNL–CF–56–9–18 (1956).
[2] J. C. WHITE, *A.S.T.M. Special Technical Publication* **238**, 27 (1958).
[3] W. J. ROSS and J. C. WHITE, Report ORNL–2627 (1958).
[4] R. A. ZINGARO and J. C. WHITE, *J. Inorg. Nucl. Chem.* **12**, 315 (1960).
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[6] J. C. WHITE and W. J. ROSS, Report ORNL–2498 (1958).
[7] J. C. WHITE and W. J. ROSS, Report ORNL–2326 (1957).
[8] G. E. BOYD and Q. V. LARSON, *J. Phys. Chem.* **64**, 988 (1960).
[9] C. K. MANN and J. C. WHITE, *Analyt. Chem.* **30**, 989 (1958).
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[11] J. C. WHITE and C. A. HORTON, *Analyt. Chem.* **30**, 1779 (1958).
[12] J. P. YOUNG and J. C. WHITE, *Talanta* **1**, 263 (1958).
[13] J. C. WHITE, *Analyt. Chem.* **31**, 1847 (1959).

Grignard reagent prepared from 1-bromoöctane and magnesium.[14] Acidic impurities such as dioctylphosphinic acid were removed from the product by shaking the mixture in petroleum ether with activated alumina, and TOPO was not finally recrystallized until shown to be free of acids by titration with sodium hydroxide using phenolphthalein as the indicator. Later experiments employed material (m.p. 50–52°C) supplied by Albright and Wilson (Mfg.) Ltd.; the two batches of TOPO had the same m.p. and mixed m.p. Cyclohexane was supplied by L. Light and Co. Ltd., and was distilled (b.p. 81°C). TOPO was always recrystallized from cyclohexane before use, and the 0·1 M solution then prepared was stored in an opaque container. Recrystallization of TOPO immediately before use was essential to obtain a clear solution.

*Preparation of plutonium (IV)*

A recently-prepared standard solution of plutonium (IV) (100 mg/ml in 10·0 N nitric acid) was used after dilution with 1·0 N nitric acid.

*Preparation of plutonium (VI)*

Plutonium entirely in the six-valent state was prepared by anodic oxidation of plutonium (IV), using the method described by HEALY and GARDNER.[15] The solution was examined for plutonium (IV) every day, and was only used if it contained no detectable amount of the latter (<0·5%).

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*Preparation of plutonium (III)*

A stock solution of plutonium (III) in hydrochloric acid was prepared by dissolving 12·5 mg of plutonium metal in 2·0 N hydrochloric acid. The solution was stabilized by addition of hydroxylamine hydrochloride. Solutions of plutonium (III) nitrate were prepared by reduction of 1·0 mg/ml plutonium (IV) nitrate in 0·5 N nitric acid with either hydroxylamine nitrate, hydroxylamine nitrate and sulphamic acid or ferrous sulphamate. After adding the reducing agent, the solutions were allowed to stand overnight before extraction with 0·1 M TOPO in cyclohexane.

*Method of equilibration*

Throughout this work 1 ml of aqueous solution was shaken for 10 min with 1 ml of organic solution (0·1 M TOPO conditioned with acid of the same strength as the aqueous solution). The degree of extraction did not change if the solutions were shaken for longer periods. The phases separated rapidly after shaking, and the aqueous layer was analysed for plutonium by α-counting. The activity of the aqueous phase before equilibration was also measured, and so gave by difference the activity of the organic phase. In the americium (III) experiments the organic and aqueous layers were both counted after equilibration. Reproducibility of results was the criterion of stability of a valency state, and the instability of plutonium (III) in nitric acid was clearly demonstrated by lack of consistent results. With the more concentrated solutions (1 mg/ml) it was possible to check some of the plutonium (IV and VI) valency states spectrophotometrically (see below).

All experiments were carried out at room temperature (about 20°C).

*Spectrophotometric measurements*

All measurements were made with a Hilger Mark II H700 Uvispek spectrophotometer, the solutions being contained in 10 mm fused silica cells with ground-glass stoppers.

*The determination of nitric acid in* 0·1 M TOPO

Five millilitre of nitric acid (0·30–11·0 N) was shaken with 5 ml of 0·1 M TOPO in cyclohexane for 10 min. After the phases had separated 4 ml of the organic layer was removed and shaken with a known excess of sodium hydroxide solution. The excess sodium hydroxide was titrated with standard hydrochloric acid using screened methyl orange as indicator.

[14] K. B. BROWN, Report ORNL–2399 (1957).
[15] T. V. HEALY and A. W. GARDNER, *J. Inorg. Nucl. Chem.* **7**, 245 (1958).

## RESULTS

Results are expressed in terms of an extraction coefficient, $E_a^0$, defined:

$$E_a^0 = \frac{\text{Concentration of plutonium in organic phase}}{\text{Concentration of plutonium in aqueous phase}} \text{ at equilibrium}$$

or

$$E_a^0 = \frac{\alpha\text{-Activity of plutonium in organic phase}}{\alpha\text{-Activity of plutonium in aqueous phase}}$$

*Extraction of plutonium (III, IV, and VI) and americium (III) nitrates*

The extraction coefficients of americium (III) and plutonium (IV and VI) nitrates from nitric acid by 0·1 M TOPO are recorded in Table 1, and plotted in Fig. 1. For comparison the extraction coefficients of chromium (VI) and uranium (VI) from the paper by WHITE[2] are also shown in Fig. 1.

In these experiments the plutonium solutions contained americium-241 formed by $\beta$-decay of plutonium-241. On account of its high specific activity and stability in the trivalent state compared with plutonium, traces of americium lead to appreciable errors in the experimentally-determined extraction coefficients. Using the extraction coefficients of americium (III), the plutonium (IV and VI) extraction coefficients were corrected for small known amounts of americium.

Over the range of acidities examined 0·1 M TOPO extracted at least 99·5 per cent of the plutonium (IV) nitrate and 99·5 per cent of the plutonium (VI) nitrate from 0·3 to 0·7 N nitric acid. The extraction of plutonium (III) nitrate from 0·2 to 2·0 N nitric acid was studied, but reproducible results could not be obtained.

*Extraction of plutonium (III, IV, and VI) chlorides*

The extraction coefficients of plutonium (III, IV, and VI) chlorides from hydrochloric acid by 0·1 M TOPO are recorded in Table 2 and plotted in Fig. 2 which also shows the extraction coefficients for chromium (VI) and uranium (VI).

No correction for americium-241 was necessary in this case as the stock solution was made from freshly-separated plutonium. At acidities less than 5·0 N, plutonium (IV and VI) chlorides were not extracted as efficiently as the nitrates. At acidities greater than 5·0 N, however, the extraction was again virtually quantitative. The extraction coefficient of plutonium (III) from hydrochloric acid increased with acid strength, but was always less than unity.

*Variation of extraction with* TOPO *concentration*

A study of the chemical nature of the complexes extracted into cyclohexane by TOPO was limited to those derived from plutonium (IV and VI) nitrates. Maximum extraction occurs at the acidity at which the complex is most stable, viz. 6·0–7·0 N for the plutonium (IV) complex and less than 1N for the plutonium (VI) complex. The acidities used in these experiments were 7·0 N (plutonium IV) and 0·69 N (plutonium VI).

Solutions containing 1 mg/ml of plutonium (IV) in 7·0 N nitric acid were shaken with varying molar excesses of TOPO in cyclohexane using a 1:1 phase ratio. The extraction coefficients are shown in Fig. 3. The formation of the extractable complex may be written as:

$$\text{Pu(IV)} + n\ \text{TOPO} \rightleftarrows \text{Pu (IV) (TOPO)}_n.$$

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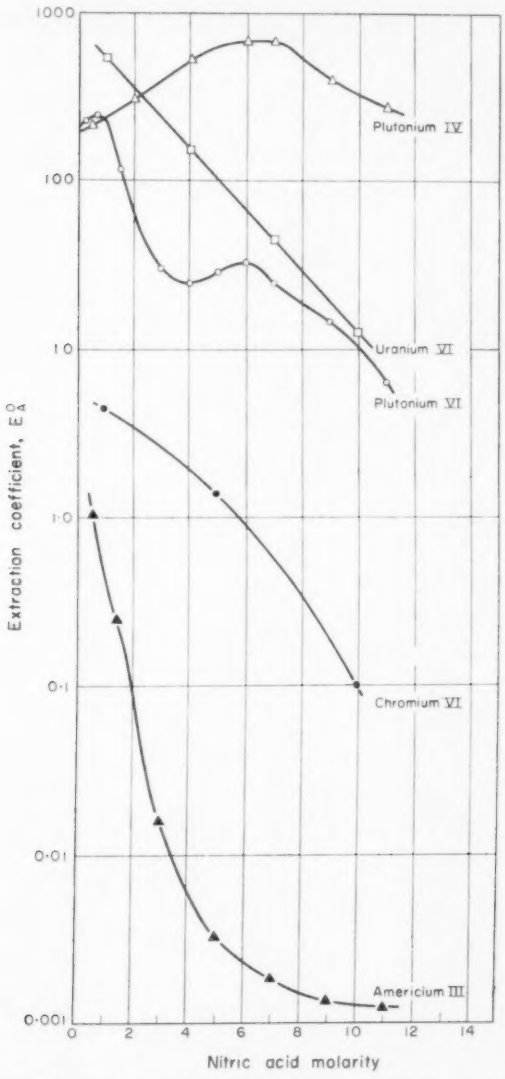


FIG. 1.—Extraction of metal ions from nitric acid by 0·1 M TOPO in cyclohexane.

ignoring the effect of complexing by nitrate ions, which also occurs. The stability constant for the reaction is then:

$$K = \frac{[\text{Pu (IV) (TOPO)}_n]}{[\text{Pu (IV)}]\,[\text{TOPO}]^n}$$

$$\therefore \qquad \log K = \log \frac{[\text{Pu (IV) (TOPO)}_n]}{[\text{Pu (IV)}]} - n \log [\text{TOPO}]$$

TABLE 1.—THE EXTRACTION OF AMERICIUM (III) AND PLUTONIUM (IV AND VI) NITRATES BY 0·1 M TOPO

| Nitric acid molarity | Extraction coefficients | | |
|---|---|---|---|
| | Am (III) | Pu (IV) | Pu (VI) |
| 0·30 | — | — | 224·9 |
| 0·50 | — | 211·0 | — |
| 0·60 | 1·03 | — | — |
| 0·69 | — | — | 238·4 |
| 1·50 | $2{\cdot}42 \times 10^{-1}$ | — | 110·4 |
| 2·00 | — | 309·6 | — |
| 3·00 | $1{\cdot}59 \times 10^{-2}$ | — | 29·3 |
| 4·00 | — | 514·0 | 25·0 |
| 5·00 | $3{\cdot}30 \times 10^{-3}$ | — | 28·3 |
| 6·00 | — | 567·1 | 32·3 |
| 7·00 | $1{\cdot}89 \times 10^{-3}$ | 567·1 | 24·2 |
| 9·00 | $1{\cdot}36 \times 10^{-3}$ | 404·9 | 14·9 |
| 11·00 | $1{\cdot}26 \times 10^{-3}$ | 272·3 | 6·4 |

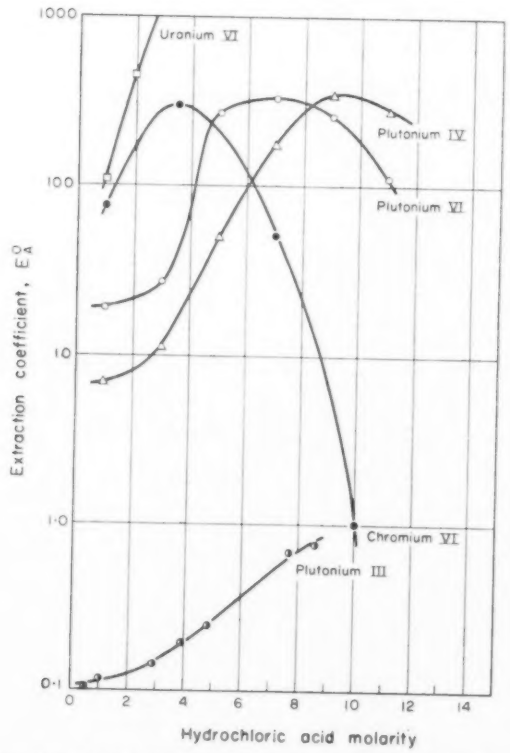


FIG. 2.—Extraction of metal ions from hydrochloric acid by 0·1 M TOPO in cyclohexane.

At equilibrium all the complex is in the organic phase, and all the uncomplexed plutonium (IV) is in the aqueous phase, so that:

$$\log K = \log E_a^0 - n \log [\text{TOPO}]$$

$$\therefore \quad \log E_a^0 = n \log [\text{TOPO}] + \log K$$

whence

$$n = \frac{\log E_a^0}{\log [\text{TOPO}]}$$

When $\log [\text{TOPO}] = 0$

$$\log K = \log E_a^0$$

TABLE 2.—THE EXTRACTION OF PLUTONIUM (III, IV, AND VI) CHLORIDES BY 0·1 M TOPO

| Hydrochloric acid molarity | Extraction coefficients | | |
|---|---|---|---|
| | Pu (III) | Pu (IV) | Pu (VI) |
| 0·43 | 0·11 | — | — |
| 1·00 | 0·12 | 7·0 | 19·1 |
| 2·90 | 0·15 | — | — |
| 3·00 | — | 11·1 | 27·2 |
| 3·85 | 0·19 | — | — |
| 4·80 | 0·25 | — | — |
| 5·00 | — | 50·4 | 271·6 |
| 7·00 | — | 172·6 | 329·4 |
| 7·65 | 0·68 | — | — |
| 8·60 | 0·76 | — | — |
| 9·00 | — | 342·6 | 250·3 |
| 11·00 | — | 280·0 | 109·7 |

The effect of nitrate complexing will be discussed later in this paper. By plotting $\log E_a^0$ vs. $\log [\text{TOPO}]$ as in Fig. 4 the slope gives a value for $n$, and the intercept on the $\log E_a^0$ axis a value for $\log K$. For the plutonium (IV) complex these values were $n = 2{\cdot}02$, $\log K = 5{\cdot}10$, $K = 1{\cdot}26 \times 10^5$.

A similar treatment of the plutonium (VI) complex extracted from 0·69 N nitric acid gave $n = 1{\cdot}98$, $\log K = 4{\cdot}50$, $K = 3{\cdot}16 \times 10^4$.

Thus the ratio of plutonium:TOPO is 1:2 in both of the complexes. The stability constants are tentative values, owing to the long extrapolation to $\log [\text{TOPO}] = 0$ (all the results are for values of $\log [\text{TOPO}]$ between $-1$ and $-2$). Fig. 4, however, shows quite definitely that the plutonium (IV) complex is more stable than the plutonium (VI) complex.

*Visible absorption spectrum of the plutonium (IV and VI)–*TOPO *complexes*

The absorption spectrum of the plutonium (IV)–TOPO complex extracted from 7·0 N nitric acid into cyclohexane was measured from 400 m$\mu$ to 1000 m$\mu$, using cyclohexane as a "blank". The region from 440 m$\mu$ to 860 m$\mu$, containing the important absorption peaks, is shown in Fig. 5 together with the spectrum of plutonium (IV) nitrate in 7·0 N nitric acid. The characteristic absorption maximum of

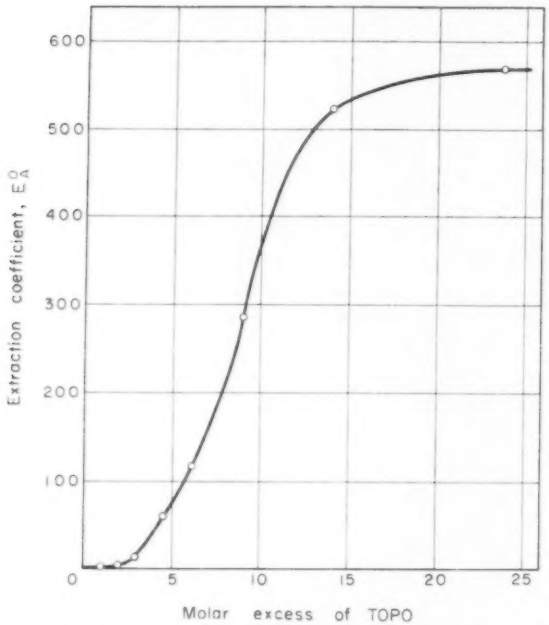


FIG. 3.—Effect of varying molar excesses of TOPO on the extraction coefficient of plutonium (IV) nitrate from 7·0 N nitric acid.

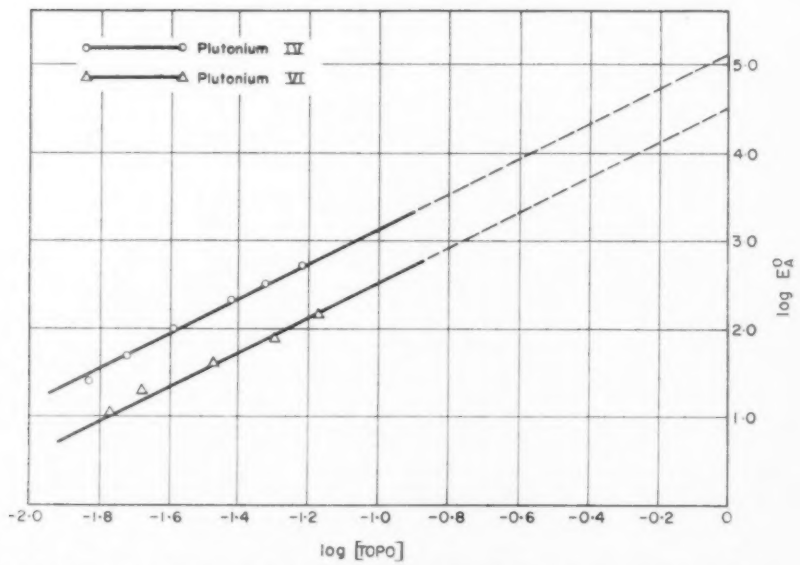


FIG. 4.—The greater stability of the plutonium (IV)–TOPO complex compared with the plutonium (VI)–TOPO complex.

plutonium (IV) nitrate at 476 m$\mu$ is shifted to 491 m$\mu$ in the TOPO complex (as also in concentrated nitric acid) and the absorption is greater throughout.

Fig. 6 shows a similar comparison of the plutonium (VI)–TOPO complex extracted from 0·69 N nitric acid and plutonium (VI) nitrate in 0·5 N nitric acid. The 830 m$\mu$

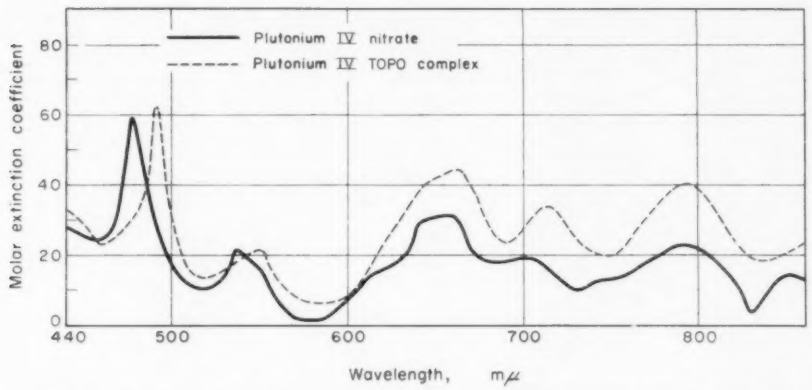


FIG. 5.—The spectra of plutonium (IV) nitrate in 7·0 N nitric acid, and of the plutonium (IV)–TOPO complex formed from 7·0 N nitric acid.

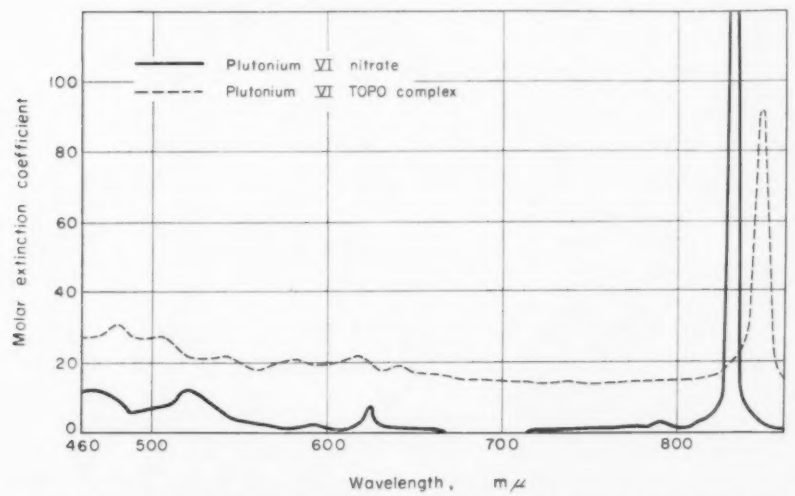


FIG. 6.—The spectra of plutonium (VI) nitrate in 0·5 N nitric acid, and of the plutonium (VI)–TOPO complex formed from 0·69 N nitric acid.

peak of plutonium (VI) nitrate is shifted to 847 m$\mu$ with some diminution of intensity. At other wavelengths the TOPO complex absorbs light more strongly than the ordinary nitrate complex.

As shown in Fig. 6 plutonium (VI) nitrate in dilute nitric acid does not absorb light in the region 670–720 m$\mu$, so that any absorption in this region can be ascribed to plutonium (IV) impurity. The absence of absorption in this region was in fact used as the criterion of purity of the valency of plutonium (VI) nitrate solutions.

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*The application of Job's "continuous variation method" to plutonium–*TOPO *complexes*

JOB's method of continuous variation[16] is widely used in the identification of complex compounds formed in solution, but fails if more than one complex is formed from the same components. By means of spectrophotometric measurements JOB's method has been improved so that several complexes in the same solution can be differentiated.[17] By measuring the optical densities of a series of solutions of the

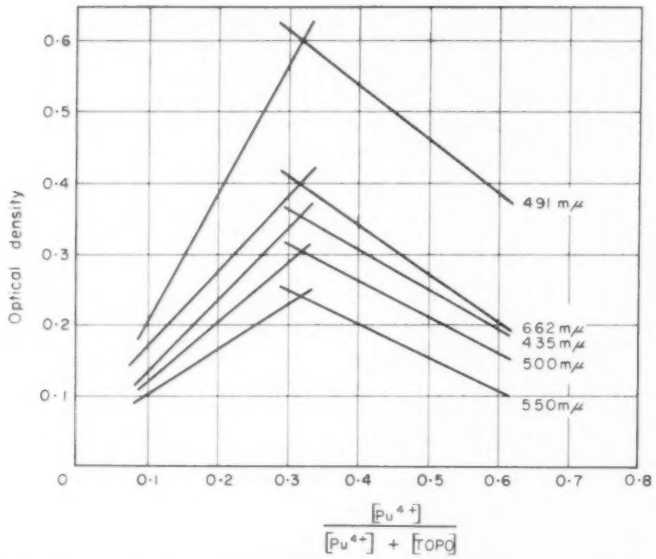


FIG. 7.—JOB's continuous variation method applied to the plutonium (IV)–TOPO complex.

same total concentration of ion plus ligand at several different wavelengths the formula of the complex may be obtained, or alternatively the existence of several complexes is apparent.

To confirm the formula of the plutonium (IV)–TOPO complex, a series of solutions of the complex was prepared by extraction of plutonium (IV) nitrate from 7·0 N nitric acid into TOPO in cyclohexane. All the solutions had the same total molarity initially (0·0336 M), but the actual plutonium (IV) and TOPO concentrations were varied. The optical densities of each solution were measured at wavelengths selected from Fig. 5—namely 435, 491, 500, 550 and 662 m$\mu$, and are plotted in Fig. 7. From this we see that

$$\frac{[\text{Pu (IV)}]}{[\text{Pu (IV)}] + [\text{TOPO}]} = 0{\cdot}33$$

$$\therefore \qquad \text{Pu (IV)} : \text{TOPO} = 1 : 2.$$

The experiment was repeated with plutonium (VI) nitrate in 0·69 nitric acid and TOPO in cyclohexane. The total concentration was 0·0336 M initially and the optical densities were measured at 410, 470, 830, 840, 845 and 850 m$\mu$. This gave

[16] P. JOB, *Ann. Chim.* **9**, 113 (1928).
[17] W. C. VOSBURGH and G. R. COOPER, *J. Amer. Chem. Soc.* **63**, 437 (1941).

Pu (VI):TOPO = 1:2, again confirming the ratio determined previously and proving that only one complex is formed.

*The extraction of nitric acid by* 0·1 M-TOPO *in cyclohexane*

The results are shown in Fig. 8. One molecule of TOPO extracts one molecule of nitric acid from 4·45 N acid. Between 2·0 N and 8·0 N nitric acid the number of

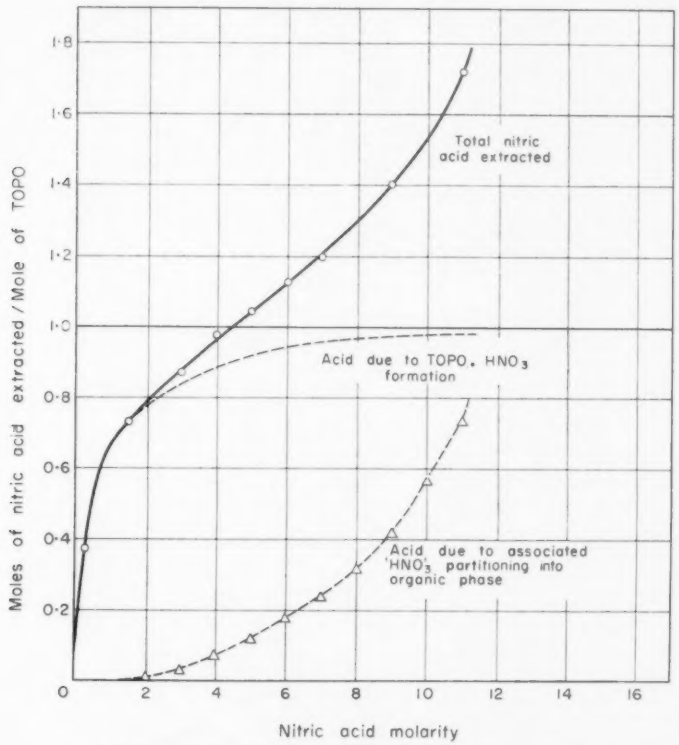


FIG. 8.—The extraction of nitric acid by 0·1 M TOPO in cyclohexane.

moles of nitric acid extracted per mole of TOPO increases linearly, but above 8·0 N the amount of acid increases very rapidly. A recent paper[18] dealing with the extraction of nitric acid by tributyl phosphate has shown that the organic phase contains only associated "$HNO_3$". At low acidities most of the nitric acid is present as the 1:1 complex TBP·$HNO_3$, while at higher acidities the effect of associated nitric acid extracted into the organic phase is considerable.

The extraction of nitric acid by 0·1 M TOPO follows a similar pattern, and the experimentally-determined curve may be divided into two portions, one due to the formation of TOPO·$HNO_3$, and the other due to the partition of associated nitric acid. ZINGARO and WHITE[4] showed that from 0 to 0·4 N nitric acid extraction is consistent with the formation of a 1:1 complex.

[18] F. L. BOYER and L. J. BIRCHER, *J. Phys. Chem.* **64**, 1328 (1960).

## DISCUSSION

### *The variation of extraction coefficient with acidity*

The shape of the extraction curve for plutonium (IV) nitrate by TOPO (Fig. 1) is a familiar one, and is characteristic of the extraction of plutonium (IV) by uncharged reagents. Electromigration[19] and ion-exchange measurements[20] show that in nitric acid plutonium (IV) may be present as a cation, an uncharged molecule or an anion, depending on the strength of the acid. There are, however, no sharply defined acidity limits for the existence of any particular species. Thus in nitric acid below 1 N, $Pu(NO_3)^{3+}$, $Pu(NO_3)_2^{2+}$ and $Pu(NO_3)_3^{+}$ are stable, whilst from 1 to 8 N uncharged $Pu(NO_3)_4$ predominates. $Pu(NO_3)_5^{-}$ is also present in increasing amounts, and at higher acidities, $Pu(NO_3)_6^{2-}$. As the extraction maximum for plutonium (IV)–TOPO coincides with the acidity corresponding to the maximum stability of uncharged $Pu(NO_3)_4$, the extractable complex could be $Pu(NO_3)_4 \cdot 2$ TOPO.

The decrease in extraction coefficient from nitric acid stronger than 7 N is due partly to the formation of anionic plutonium (IV) complexes and partly to the competition between plutonium (IV) and nitric acid for TOPO. Above 8 N the concentration of associated "$HNO_3$" in nitric acid increases rapidly[20] so displacing the equilibrium to the right in the following equation:

$$TOPO + HNO_3 \rightleftarrows TOPO \cdot HNO_3$$

Consequently at high acidities there will be less TOPO available for complexing plutonium (IV).

In the case of plutonium (VI) a similar maximum occurs in extraction from 6·0 N nitric acid. The principal maximum, however, is from 0·69 N nitric acid, and the reason for this is not clear. The removal of acidic impurities from TOPO, ensures that the first extraction peak (apparently hydrogen ion-dependent) cannot be due to the formation of a plutonium (VI)–dioctylphosphinate complex. Furthermore, the plutonium (VI) concentration ($4{\cdot}2 \times 10^{-3}$ M) is too high for the observed effect to be caused by reaction of plutonium (VI) with traces of impurity. In the extraction of plutonium (IV and VI) nitrates by tributyl phosphate,[21] another neutral reagent, the two curves show the same simple peak shape, plutonium (VI) extraction being the lower.

The extraction of plutonium (IV and VI) chlorides (Fig. 2) is apparently similar to that described for plutonium (IV) nitrate. The low extraction of plutonium (III) from chloride solutions is characteristic of trivalent actinides. The weak complexing of plutonium (III) by chloride ions[22] is insufficient to form uncharged $PuCl_3$, which may be necessary for quantitative extraction.

### *The instability of plutonium (III) in nitric acid*

The instability of plutonium (III) in nitric acid is well known and DUKES[23] has studied the oxidation of plutonium (III) by nitrous acid. CARLESON[24] has shown

[19] C. K. MCLANE, J. S. DIXON and J. C. HINDMAN. *The Transuranium Elements* (Edited by G. T. SEABORG, J. J. KATZ and W. M. MANNING), NNES, Division IV, Plutonium Project Record, Vol. 14B, p. 364. McGraw-Hill, New York (1949).
[20] J. BROTHERS, R. G. HART and W. G. MATHERS, *J. Inorg. Nucl. Chem.* **7**, 85 (1958).
[21] G. F. BEST, H. A. C. MCKAY and P. R. WOODGATE, *J. Inorg. Nucl. Chem.* **4**, 315 (1957).
[22] M. WARD and G. A. WELCH, *J. Inorg. Nucl. Chem.* **2**, 395 (1956).
[23] E. K. DUKES, *J. Amer. Chem. Soc.* **82**, 9 (1960).
[24] G. CARLESON, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, Vol. 17, p. 111. United Nations (1959).

that the partition coefficient of plutonium (III) between nitric acid and 36 per cent tributyl phosphate (TBP) in olefin-free kerosene depends on the reducing and stabilizing agents used. Other extraction systems for plutonium (III) in nitric acid are:

| Extracting reagent | Strongest acid used | Reference |
|---|---|---|
| 100% TBP | 2·5 N | (25) |
| 20% TBP in odourless kerosene | 5·0 N | (21) |
| 10% Tri-*n*-octylamine in xylene | 8·0 N | (26) |

Each author claimed to use the strongest acid in which plutonium (III) is stable. This discrepancy may be due to the use of different solvents and extracting agents. As described earlier, pure plutonium (III) could not be extracted with TOPO from nitric acid at any acidity, partial oxidation to plutonium (IV) always occurred. This is unfortunate, as stable plutonium (III) with a low extraction coefficient would be of considerable analytical importance.

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*Analytical applications*

In determining the solvent extraction properties of plutonium and americium ions by TOPO, the advantages and limitations of TOPO in the analysis of plutonium and americium became apparent. The single disadvantage is the ease with which TOPO extracts the higher valency states of other actinide ions (e.g. uranium (VI) and thorium (IV)), so making a separation from plutonium (IV and VI) difficult. On the other hand, when the trivalent actinide is stable as in the case of americium, separation from plutonium (IV and VI), uranium (VI), and thorium (IV) is a simple matter. In addition TOPO could simplify the separation of plutonium from most metal ions other than the actinides, and it is to be recommended for this purpose. Extraction with TOPO is nearly always quantitative, and a large aqueous to organic phase ratio may be used.[10]

[25] G. F. Best, E. Hesford and H. A. C. McKay, *J. Inorg. Nucl. Chem.* **12**, 136 (1960).
[26] W. E. Keder, J. C. Sheppard and A. S. Wilson, *J. Inorg. Nucl. Chem.* **12**, 327 (1960).

J. Inorg. Nucl. Chem., 1961, Vol. 21, pp. 108 to 123. Pergamon Press Ltd. Printed in Northern Ireland

# HETEROGENEOUS EQUILIBRIA IN THE SYSTEM WATER–NITRIC ACID–DI-*n*-BUTYL PHOSPHATE

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**Abstract**—Di-*n*-butyl phosphate solutions of nitric acid were investigated to determine the stoicheiometry and stability of the molecular-association compounds formed in the heterogeneous reaction between these two components. From the variation of the physical–chemical properties of the organic layers, and from the variation of the distribution of $HNO_3$, the empirical formulae of the extracted species were found to be close to $(DBP{\cdot}H_2O)_2{\cdot}HNO_3$, $DBP{\cdot}H_2O{\cdot}HNO_3$ and $DBP{\cdot}H_2O{\cdot}(HNO_3)_2$. Electrical conductivity and viscosity measurements showed that $HNO_3$ in undiluted DBP is substantially ionized when in equilibrium with dilute aqueous solutions of the acid. The effect of adding an inert diluent to the organic phase was studied. The solubility of DBP in water and aqueous nitric acid solutions was measured for a range of DBP concentrations. With a reasonable assumption as to the extraction mechanism involved, an attempt was made to calculate the formation constants of the individual species.

IN view of the well established application of di-*n*-butyl phosphate (DBP) and other dialkyl phosphoric acids to the extraction of metals from aqueous nitric acid systems, it is somewhat surprising that data for nitric acid–dialkyl phosphoric acid interactions have not hitherto been available. It was therefore considered of interest to study the solute–solvent interaction in the ternary system water–nitric acid–di-*n*-butyl phosphate. This study is devoted particularly to the physical-chemical behaviour of the organic phase.[1–4] The volume change of the organic layer, its viscosity, density and conductivity were found to be dependent upon its acid content. These data, together with the extraction ratio of the acid and the organic water content provided considerable evidence as to the state of solvation and of hydration of the acid in the organic phase.

The di-*n*-butyl ester of orthophosphoric acid has been extensively used to extract uranium[5–11] and other elements of the actinium series,[12–14] the lanthanons,[14,15]

[1] A. S. KERTES, *J. Inorg. Nucl. Chem.* **14**, 104 (1960); **12**, 377 (1960).
[2] A. S. KERTES and V. KERTES, *Canad. J. Chem.* **38**, 612 (1960).
[3] A. S. KERTES and V. KERTES, *J. Appl. Chem.* **10**, 287 (1960).
[4] A. S. KERTES and M. HALPERN, *J. Inorg. Nucl. Chem.* **16**, 308 (1961).
[5] B. J THAMER, Report LA–1996 (1956).
[6] T. V. HEALY and J. KENNEDY, *J. Inorg. Nucl. Chem.* **10**, 128 (1959).
[7] D. DYRSSEN and F. KRAŠOVEC, *Acta Chem. Scand.* **13**, 561 (1959).
[8] G. I. CATHERS, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva* 1955, Vol. 7, p. 490. United Nations (1956).
[9] W. W. MORGAN, W. G. MATHERS and R. G. HART, *Industr. Engng. Chem.* **51**, 817 (1959).
[10] G. R. PRICE, R. J. FERRETTI and S. SCHWARTZ, *Analyt. Chem.* **25**, 322 (1953).
[11] P. G. M. BROWN, J. M. FLETCHER, C. J. HARDY, J. KENNEDY, D. SCARGILL, A. G. WAIN and J. L. WOODHEAD, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, United Nations, Geneva*, 1958, Vol. 17, p. 118. United Nations (1959).
[12] D. F. PEPPARD, G. W. MASON, W. J. DRISCOLL and S. MCCARTY, *J. Inorg. Nucl. Chem.* **12**, 141 (1959).
[13] B. V. SHEVCHENKO, V. A. MIHAILOV and Y. P. ZAVALISKII, *Zh. Neorg. Khim.* **3**, 1956 (1958).
[14] D. DYRSSEN and D. H. LIEM, *Acta Chem. Scand.* **14**, 1100, 1960.
[15] G. DUYCKAERTS, PH. DRÈZE and A. SIMON, *J. Inorg. Nucl. Chem.* **13**, 332 (1960).

and also for the separation of zirconium from niobium[11,16,17] and of strontium from yttrium.[18] In addition to these results on the extraction of various metallic species, two groups have published papers on the solubility, distribution, dissociation and dimerization of DBP in different organic solvent systems. DYRSSEN *et al.*[19,20] have measured the distribution ratio of DBP between several organic solvents and diluted perchloric and nitric acid solutions, and have in addition determined the dimerization constant of DBP in organic solvents. HARDY and SCARGILL[21] determined the solubilities of DBP in water and aqueous nitric acid solutions, and measured the distribution coefficient of DBP between 1 M nitric acid and kerosene, benzene and kerosene–TBP mixtures.

## EXPERIMENTAL

### *Materials*

Di-*n*-butyl phosphate was prepared by purifying materials supplied by Albright & Wilson, London. According to the manufacturer (i) the product contained 95–97 per cent of the dibutyl ester, the balance being principally mono-butyl phosphate; (ii) the pure product has b.p. 116–118° at 0·01 mm; (iii) the refractive index is 1·425 and specific gravity 1·06. Our purification treatment was identical with that described by HARDY and SCARGILL[22]. Two purification cycles left the DBP product as a pale yellow viscous liquid. Electrometric titration curves in ethanol with $pK = 1{\cdot}72$, suggest that the purified product contains a non-acidic impurity, but must be at least 96 per cent pure.

Baker "Analyzed Reagents" grade nitric acid and carbon tetrachloride were used without further purification; all other reagents were also of the highest purity. DBP solutions in $CCl_4$ were prepared by weight. Initial aqueous solutions of nitric acid were prepared by dilution, and standardized potentiometrically.

### *Solubility measurements*

One hundred ml of water or aqueous nitric acid solutions were mechanically shaken with equal volumes of undiluted or diluted DBP for at least 15 min in a constant-temperature bath at 27° ± 0·1°C. Samples of the aqueous phases were withdrawn through paper and cotton filters, centrifuged and analysed for DBP by the method described below. The values are probably accurate at least to within ±5 per cent.

### *Equilibrium and volume change measurements*

The equilibration of the phases is accompanied by swelling of the organic phase due to the solubility in it of aqueous nitric acid. Five ml of the relatively lighter phase were carefully added to 5 ml of the opposite phase in a 10 ml centrifuge tube graduated to 0·1 ml, and the interface- and air-menisci immediately noted. The stoppered tubes were then violently shaken for 15 min in a mechanical shaker. Equilibrium was always reached within a few minutes. Except with samples of the highest concentrations of $HNO_3$ and DBP, when a tendency for emulsion formation was noted, excellent phase separation was ensured after 1 min of centrifugation at full speed in an International Clinical Centrifuge. The menisci at equilibrium were read to within ±0·025 ml, and the volume changes calculated. All the results given are an average of at least three determinations. The three identical samples were poured into one 50 ml centrifuge tube, centrifuged, and samples of each phase reserved for analysis. All experiments were carried out at room temperature (22–27°C).

### *Analytical procedures*

Aliquots of both phases were immediately diluted, the organic phase with a 1:3 water–ethanol

[16] E. M. SCADDEN and N. E. BALLOU, *Analyt. Chem.* **25**, 1602 (1953).
[17] E. K. DUKES, Report DP–250 (1957).
[18] D. DYRSSEN, *Acta Chem. Scand.* **11**, 1277 (1957). D. DYRSSEN and S. EKBERG, *Acta Chem. Scand.* **13**, 1909 (1959).
[19] D. DYRSSEN, *Acta Chem. Scand.* **11**, 1771 (1957).
[20] D. DYRSSEN and D. H. LIEM, *Acta Chem. Scand.* **14**, 1091 (1960).
[21] C. J. HARDY and D. SCARGILL, *J. Inorg. Nucl. Chem.* **11**, 128 (1959).
[22] C. J. HARDY and D. SCARGILL, *J. Inorg. Nucl. Chem.* **10**, 323 (1959).

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mixture. The concentrations of the acids, $HNO_3$ and DBP, were determined potentiometrically using a Beckman Zeromatic pH-meter. The concentrations of individual acids were obtained by differences in the alkali equivalents, and the equivalents calculated from phosphorus determinations in the samples. For higher DBP and $HNO_3$ concentrations only the equilibrium aqueous phase was analysed, and the acid content of the organic phase was obtained by difference, corrections being made for the solubility of the ester in the aqueous phase. In several cases, a test for material balance was also made.

Analyses for total phosphorus involved hydrolysis of the ester with fuming $H_2SO_4$ and $HNO_3$, and subsequent colorimetric determination of phosphomolybdate blue[23] using a Beckman Model B Spectrophotometer.

The water content of the organic phase was found by using the Karl Fischer Reagent and the dead-stop end-point method as determined with a Fisher Titrimeter. The reagent was standardized against a known "Fisher Scientific Reagents" solution of water in methanol, and checked against AnalaR grade sodium tartrate dihydrate.

*Physical–chemical analyses*

Density, viscosity and conductivity measurements of the homogeneous organic layers were performed immediately after equilibration and separation according to the procedure described previously.[1] A thermostatic water-bath at 27 ± 0·1° was used for these determinations.

## RESULTS AND DISCUSSION

*Solubility of DBP in water and aqueous nitric acid solutions*

The solubility of DBP in water at 27°C, calculated as a function of its mole fraction in $CCl_4$ diluent, is shown in Fig. 1. On a molar basis, the solubility of DBP in water rises from 0·022 M at 2% DBP in $CCl_4$ to 0·071 M at 96% DBP content in the organic phase. The general shape of the solubility isotherm is similar to that of TBP in the same diluent.[24] To explain the solubility curve one must take into account the extent of molecular association of DBP with the carrier solvent, as this influences the extent of dimerization of DBP in the organic diluent. The formation of a 1 : 1 association compound between DBP and $CCl_4$, which may explain the solubility break point at a mole fraction of 0·5, is contra-indicated by the high dimerization constant $K_{dimer} = 10^{6\cdot49}$, of DBP in $CCl_4$, as found by DYRSSEN and LIEM[20]. The almost linear increase in solubility when the mole fraction of DBP exceeds 0·5 is in accordance with the findings of DYRSSEN and LIEM[20] that the distribution constant of the dimerized DBP is independent of the composition of the organic phase. This is shown by the curve in Fig. 2, where log $E^{\circ}_{aDBP}$ is plotted against log $[DBP]_a$, where $[DBP]_a$ is the ester molarity in water.

From DYRSSEN'S[19] values of the dissociation and dimerization constants of DBP, HARDY and SCARGILL[21] calculated the contributions of each individual species to the overall solubility of DBP in water: the ion $(BuO)_2POO^-$ contributes about 56 per cent, the unionized DBP monomer about 28 per cent and the unionized $(DBP)_2$ dimer the remaining 16 per cent. The formation of DBP–$CCl_4$ association compounds, and the low dielectric constant of $CCl_4$ both tend, on the other hand, to decrease the ionization of DBP,[25] and consequently to lower its water solubility. The linear increase in the extraction ratio of DBP with increasing content in $CCl_4$ up to a 1:1 mole ratio can be explained by the progressive DBP–$CCl_4$ compound formation which favours the organic phase. Once the diluent has been completely used up to

[23] J. KENNEDY and S. S. GRIMLEY, AERE/CE/R–968 (1952).
[24] W. F. JOHNSON and R. L. DILLON, Report HW–29086 (1953).
[25] C. F. BAES, Jr., Report ORNL–2737 (1959).

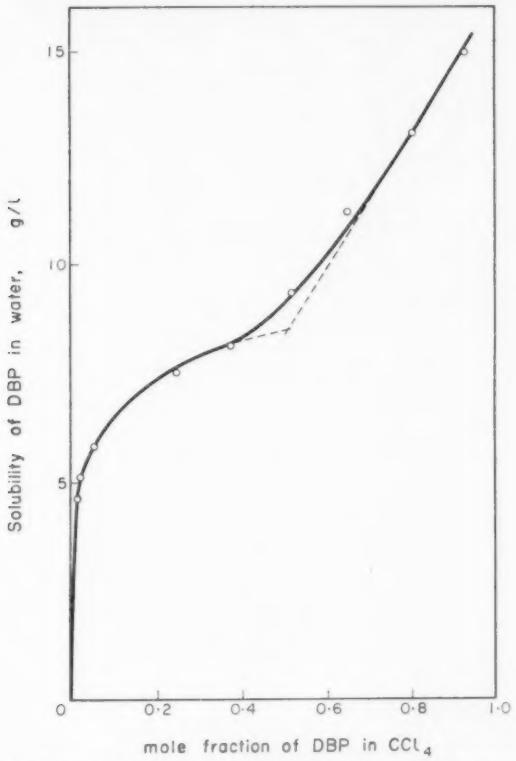


FIG. 1.—Solubility of DBP in water at 27° as a function of its mole fraction in $CCl_4$.

form the 1 : 1 association compound, addition of further DBP results in "ideal solution" behaviour, the extraction ratio remaining approximately constant and independent of the DBP concentration in the organic mixture.

An alternative explanation of the greatly increased solubility of DBP at higher concentrations beyond ~3 M in $CCl_4$ can be based on a partial polymerization beyond the dimer.[20,25,26] The trimer, owing to its more open structure, might be expected to interact more strongly with water.[25]

Fig. 3 shows the solubility isotherm, at 27°C, of DBP in aqueous nitric acid solutions for various initial DBP concentrations in the carbon tetrachloride phase. In 0·1 M $HNO_3$ the solubility of DBP drops to less than half its value in water alone. There is an overall decrease in the solubility of DBP in nitric acid up to concentrations of about 8 M $HNO_3$. Beyond this concentration the solubility begins to rise sharply and even exceeds the solubility in water alone. Some of our determinations of the solubility of undiluted DBP are new; in other cases there is fair agreement with values reported from Harwell[21], except that a minimum solubility is noted in the range from 4 to 8 M $HNO_3$, no such measurements having been reported previously. Neither were solubility measurements reported in the presence of diluent.

The molar activity coefficient ($f$) of DBP in aqueous nitric acid solutions was

[26] C. F. BAES, Jr. and H. T. BAKER, *J. Phys. Chem.* **64**, 89 (1960).

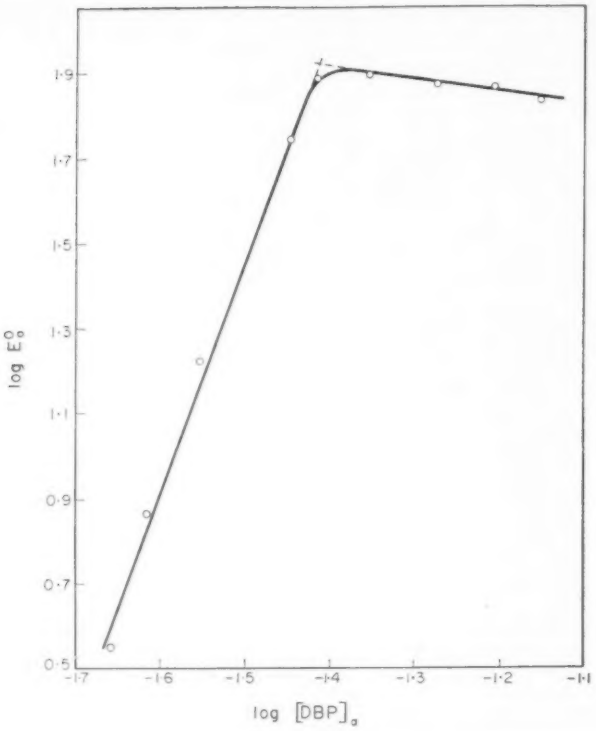


FIG. 2.—The extraction ratio of DBP between water and $CCl_4$ as a function of the DBP content in the equilibrium aqueous phase.

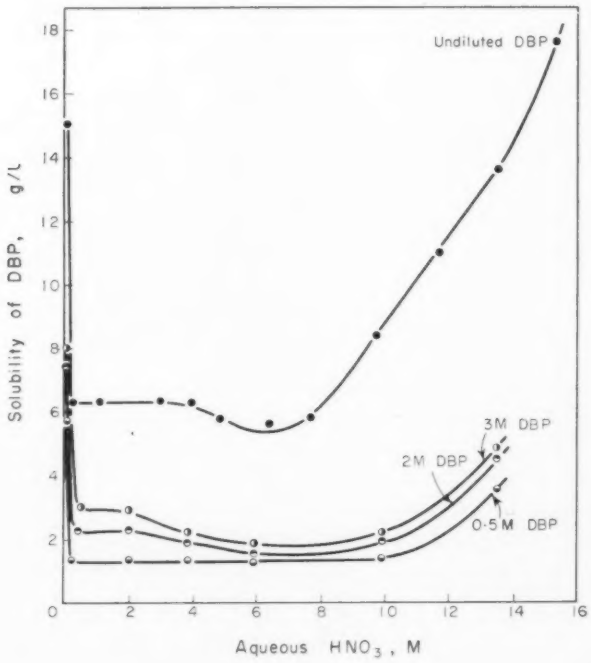


FIG. 3.—Solubility of DBP in aqueous nitric acid solutions at 27°.

calculated from the equation[27,28] $f = S_0/S$, where $S_0$ is the molar solubility of DBP in pure water and $S$ is its molar solubility in the nitric acid solution. In the dilute concentration range of the acid, where the conditions of the Setchenov equation are valid, the salting coefficient $k_s$, for all the DBP concentrations investigated, has a value close to zero, with a slight tendency to a negative value, this being a salting-in effect. The value of $k_s$ found for TBP in an identical system[28] is 0·015.

HARDY and SCARGILL[21] have interpreted the solubility of DBP in $HNO_3$ in terms of dissociation and dimerization of DBP. Although we agree with the authors that the decreased solubility results from a repressed dissociation of DBP in the presence of an increased hydrogen-ion concentration, we believe that complete interpretation of the solubility isotherms shown in Fig. 3 is clearly not a simple matter. No correct explanation can be offered without taking into account the solute–solvent interaction in the organic phase. This research revealed, as will be shown later, the existence of three association compounds between DBP and $HNO_3$ in the organic phase when it is in equilibrium with aqueous nitric acid solutions of varying concentrations. For concentrations of acid up to ~9 M in the initial aqueous solution (see Fig. 8), the main compound in the DBP phase has the gross formula $(DBP.H_2O)_2.HNO_3$; for concentrations between 9 M and 13·5 M the prevailing species has the composition $DBP.H_2O.HNO_3$, and at the highest initial acid concentrations investigated the compound $DBP.H_2O.(HNO_3)_2$ is formed. The first compound seems to be very slightly soluble, even less soluble than the hydrated DBP-dimer $(DBP.H_2O)_2$, the "free" DBP compound which exists at low acid concentrations in the organic phase. The rapid overall increase in the aqueous DBP content from an initial aqueous acidity of about 9 M $HNO_3$ is connected with the formation of the compound $DBP.H_2O.HNO_3$. The even sharper increase in the DBP solubility from about 13·5 M $HNO_3$ must be explained by the formation of the more soluble third association complex in the organic phase.

*Distribution of nitric acid between water and undiluted di-n-butyl phosphate and the physical–chemical data for the organic layers*

Table 1 shows the nitric acid concentration in the initial aqueous solutions and in both aqueous and organic equilibrium layers. Column 6 shows the extraction ratio, $E^{\circ}_{a_{HNO_3}}$, and the last column the acid : extractant ratio in the equilibrium organic phase. Although the initial amount of DBP was constant throughout these measurements, and corresponded to 24·25 mmole in 5 ml of the initial organic phase, when calculating the $HNO_3$/DBP ratio corrections were made for the solubility losses of DBP in nitric acid at corresponding acid concentrations, as previously determined. On the other hand, no hydrolysis corrections were made for DBP, although it is well known that this occurs, since from results obtained it was thought feasible to ignore this relatively small effect. Fig. 4 shows the plot of the mole ratio $[HNO_3]_0/[DBP]_0$ against the acidity in the initial aqueous solution. Fig. 5 shows the extent to which mutual miscibility of the layers is dependent upon the mole ratio $[HNO_3]_0/[DBP]_0$ in the organic phase. When the viscosities and specific conductance of the equilibrium organic phases are plotted against the mole ratio $[HNO_3]_0/[DBP]_0$, the curves shown in Figs. 6 and 7 are obtained.

[27] W. F. MCDEVIT and F. A. LONG, *J. Amer. Chem. Soc.* **74**, 1773 (1952).
[28] C. E. HIGGINS, W. H. BALDWIN and B. A. SOLDANO, *J. Phys. Chem.* **63**, 113 (1959).



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TABLE 1.—DISTRIBUTION OF NITRIC ACID BETWEEN WATER AND UNDILUTED DI-*n*-BUTYL PHOSPHATE AS A FUNCTION OF THE ACID CONCENTRATION IN THE INITIAL AQUEOUS SOLUTION

| No. of Exp. | $HNO_3$(mole/l) | | | Volume of the equilib. organic phase* | $E^{\circ}_{a_{HNO_3}}$ | $(HNO_3)_0/(DBP)_0$ mole ratio |
|---|---|---|---|---|---|---|
| | Initial aqueous solution $(HNO_3)_i$ | Equilib. aqueous phase $(HNO_3)_a$ | Equilib. organic phase $(HNO_3)_0$ | | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 1 | 0·100 | 0·087 | 0·018 | 5·35 | 0·201 | 0·004 |
| 2 | 0·200 | 0·186 | 0·025 | 5·35 | 0·135 | 0·005 |
| 3 | 0·490 | 0·476 | 0·044 | 5·35 | 0·093 | 0·009 |
| 4 | 0·978 | 0·925 | 0·117 | 5·40 | 0·127 | 0·025 |
| 5 | 1·971 | 1·770 | 0·317 | 5·40 | 0·179 | 0·068 |
| 6 | 2·932 | 2·532 | 0·558 | 5·40 | 0·220 | 0·119 |
| 7 | 3·896 | 3·276 | 0·840 | 5·45 | 0·256 | 0·181 |
| 8 | 4·842 | 4·046 | 1·082 | 5·50 | 0·268 | 0·234 |
| 9 | 5·864 | 4·931 | 1·336 | 5·55 | 0·272 | 0·292 |
| 10 | 7·747 | 6·493 | 1·848 | 5·65 | 0·285 | 0·426 |
| 11 | 8·800 | 7·397 | 2·140 | 5·70 | 0·289 | 0·481 |
| 12 | 9·651 | 8·201 | 2·333 | 5·75 | 0·285 | 0·528 |
| 13 | 10·61 | 8·946 | 2·704 | 5·85 | 0·303 | 0·623 |
| 14 | 11·47 | 9·680 | 3·051 | 5·95 | 0·315 | 0·716 |
| 15 | 12·28 | 10·43 | 3·478 | 6·05 | 0·333 | 0·831 |
| 16 | 13·54 | 11·42 | 4·091 | 6·20 | 0·358 | 0·993 |
| 17 | 14·03 | 11·74 | 4·255 | 6·30 | 0·361 | 1·052 |
| 18 | 14·47 | 12·19 | 4·455 | 6·40 | 0·366 | 1·108 |
| 19 | 14·85 | 12·51 | 4·670 | 6·50 | 0·373 | 1·192 |
| 20 | 15·39 | 13·03 | 4·972 | 6·70 | 0·381 | 1·332 |

* Initial volume of each phase 5 ml.

Each of the curves shown in Figs. 4–7 shows three intersections between straight lines of different slopes. The breaks appear at the following ratios of $[HNO_3]_0/[DBP]_0$: 1, 0·5 and roughly 0·12, which were interpreted as indicating the molar composition of the extracted species, i.e. the solvation number of the acid passing into the DBP layer. Comparison of the physical–chemical behaviour of the organic phase at different acidities suggested the existence of two well-defined compounds between DBP and $HNO_3$. The ratio $[HNO_3]_0/[DBP]_0$ is 0·5 in the first compound and unity in the second, and the simple molecular-association models can be written as $[(DBP)_2.HNO_3]$ and $[DBP.HNO_3]$ respectively. The first intersection in Figs. 4–7 was attributed to the dissociation of nitric acid in the hydrated DBP (see below).

With the aid of the empirical formulae for the compounds in the organic phase, based on the physical–chemical analyses, and on the reasonable assumption that for each initial aqueous acidity only two species exist in the organic phase, with a total concentration which is essentially equal to the nitric acid content of the phase (as all other possible $HNO_3$ species are considered to be present only in extremely small concentrations) Fig. 8 was constructed from the data of Table 1, presenting the different molecular species. The concentration of DBP-dimer, $(DBP)_2$, was calculated from the difference between the nitric acid present in the organic phase and the total DBP.

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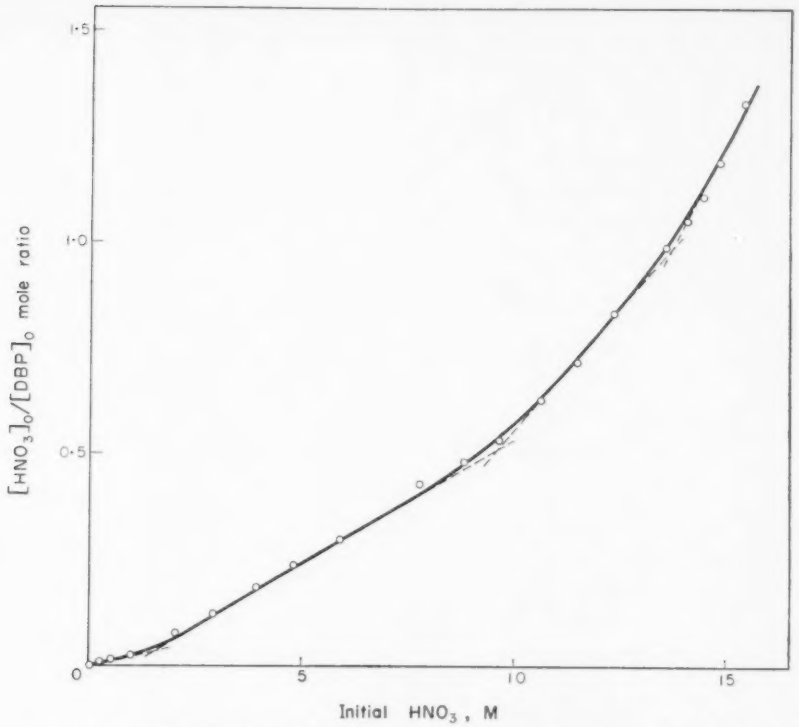



FIG. 4.—$[HNO_3]_0/[DBP]_0$ mole ratio in the organic phase of undiluted DBP as a function of the nitric acid concentration in the initial aqueous solution.

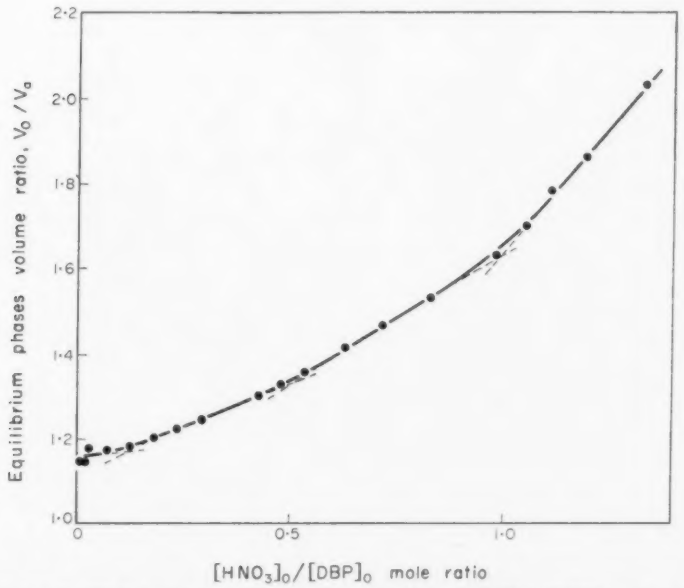



FIG. 5.—Equilibrium phase volume ratios as a function of $[HNO_3]_0/[DBP]_0$ mole ratio in the organic phase of undiluted DBP system.

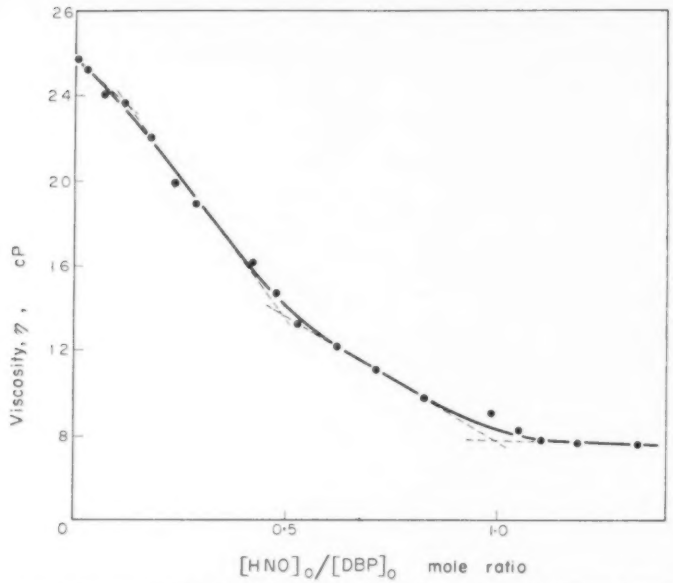



FIG. 6.—Viscosities of the equilibrium organic phase vs. the $[HNO_3]_0/[DBP]_0$ mole ratio of the undiluted DBP system.

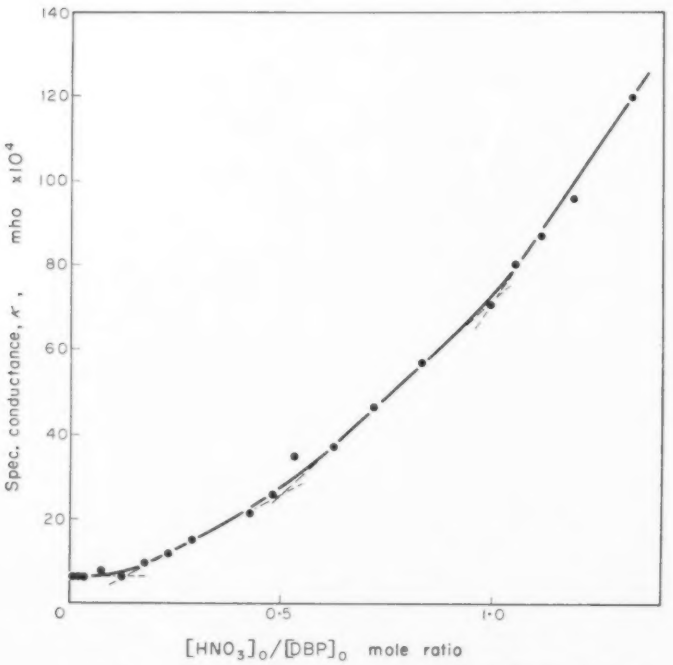



FIG. 7.—Specific conductance of the equilibrium organic phase vs. $[HNO_3]_0/[DBP]_0$ mole ratio of the undiluted DBP system.

The quantity of $(DBP)_2.HNO_3$ formed in the organic phase up to a $[HNO_3]_0/[DBP]_0$ ratio of 0·5, was equal to the quantity of nitric acid in the organic phase. The formation of $DBP.HNO_3$ starts beyond the above ratio, while the amount of $(DBP)_2 \cdot HNO_3$ consequently decreases. It must, however, be taken into consideration that this compound might be present even before the ratio of 0·5 is exceeded, in view of the fact that the concentrations of the species are probably regulated by a chemical equilibrium. The amounts of $DBP.HNO_3$ were calculated from the $HNO_3$ content of the organic phase above the ratio of 0·5, by subtracting this amount from the total

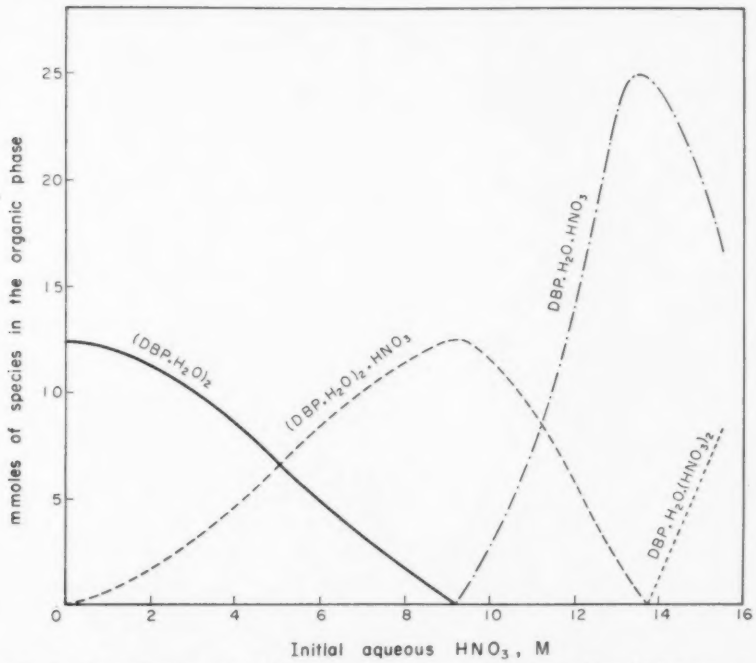



FIG. 8.—Concentration of the different molecular species in the undiluted DBP system as a function of the nitric acid molarity in the initial aqueous solution.

number of moles of DBP. At a $[HNO_3]_0/[DBP]_0$ ratio of unity it was assumed that no other compounds were present in the organic phase except $DBP.HNO_3$. The excess of $HNO_3$, with respect to the ratio of unity, represents the quantity of $DBP \cdot (HNO_3)_2$ formed.

In fact, the calculation of the equilibrium constants involved must prove the above simple state in the organic phase.

*Hydration and ionization of nitric acid in the organic phase*

The water uptake of DBP in equilibrium with water and aqueous solutions of nitric acid is shown in Fig. 9, which gives the mmoles of water in the DBP phase as a function of the $HNO_3$ molarity in the organic layer. The straight line drawn with zero slope indicates that the presence of nitric acid does not increase the water solubility. The water content of undiluted DBP in equilibrium with pure water is about 4·55 M, which is exactly the molarity of water-saturated undiluted DBP. Although

the accuracy of our Karl Fischer titrations was believed to be at least ±5 per cent, several points show a drastic departure from the line drawn. Nevertheless, these deviations, which in a few cases are as large as 10 per cent, are hardly sufficient to cause us to believe that the water uptake of undiluted DBP in equilibrium with aqueous nitric acid solutions is significantly different from that observed on its saturation with water.

Although we must be very cautious in drawing conclusions about the water content of the organic phase in partition equilibria, the curve presented in Fig. 9 presents a weighty argument for two very important points:

(1) the hydration of DBP and the stability of the hydrated species, and
(2) the constitution of the extractable nitric acid molecules.

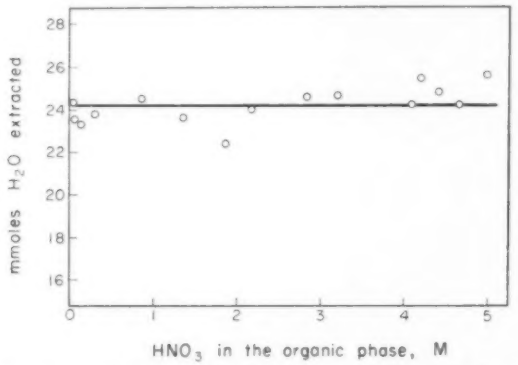
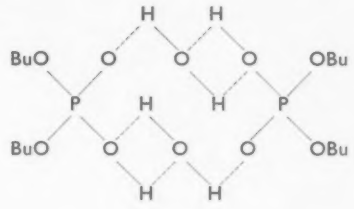



FIG. 9.—Millimoles of $H_2O$ extracted vs. the molarity of nitric acid in the undiluted organic phase.

It is not difficult to maintain the view that dibutyl phosphate forms a monohydrate in equilibrium with aqueous solutions, probably by hydrogen bonding. It is undoubtedly significant that the amount of water in the organic phase remains practically unchanged as the amount of the acid extracted increases. This is the complete opposite of the corresponding TBP system, where a gradual displacement of water, from the complex TBP.$H_2O$ takes place as extraction of $HNO_3$ into TBP proceeds.[29–31] No such displacement of water takes place, however, when acids other than nitric are extracted into TBP.$H_2O$, as shown in previous works from this and other laboratories.[1–4,32–34] The stability of the TBP-monohydrate in the presence of concentrated acids such as HCl, HBr and $HClO_4$, was previously[3] explained as being due to the same water molecule being doubly hydrogen-bonded to the same oxygen atom as acceptor. In line with this reasoning the DBP-monohydrate seems to be more stable than that of TBP. Although experiments carried out on this point cannot determine whether dimerized DBP molecules remain in the water-saturated solution or whether the new hydrated DBP species formed are monomers, the absence of ions

[29] K. ALCOCK, S. S. GRIMLEY, T. V. HEALY, J. KENNEDY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 39 (1956).
[30] D. G. TUCK, *J. Chem. Soc.* 2783 (1958).
[31] L. DAMIANI and V. FATTORE, *Energia Nucl.* **6**, 793 (1959).
[32] W. H. BALDWIN, C. E. HIGGINS and B. A. SOLDANO, *J. Phys. Chem.* **63**, 118 (1959).
[33] H. IRVING and D. N. EDGINGTON, *J. Inorg. Nucl. Chem.* **10**, 306 (1959).
[34] E. HESFORD and H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* **13**, 156 (1960).

in appreciable quantity in this water-saturated undiluted DBP solution would suggest that the dimer is not broken down at this stage, but that the real molecular compound is a dimer-dihydrate. This compound is not ionic, but a hydrogen-bonded complex, represented as




similar in nature to that formed between tributyl phosphate and water.

Although the picture of the molecular constitution of nitric acid in aqueous solutions is not particularly precise in detail,[35–37] and although the exact composition of the species varies widely with the concentration of the aqueous solution,[38] the assumption can nevertheless be made on the basis of the curve shown in Fig. 9 that the extractable nitric acid molecule is unhydrated throughout the nitric acid concentration range investigated.

As far as the ionization of nitric acid in the organic phase is concerned, it seemed probable that the acid would be substantially unionized in DBP, as in the similar TBP system. A rough estimation of the degree of ionization is generally[1–3,33,34] calculated employing Walden's relation $\lambda\eta/60$. Unlike similar TBP systems, in which the measured conductance was entirely due to the solute species, in the system under consideration an appropriate solvent conductance correction[39] has to be applied, as the hydrated ester has a specific conductance of about $6 \times 10^{-4}$ mhos, which is not appreciably increased when the organic phase contains up to about 0·1 M nitric acid. Evidently, Walden's rule in its simple form is not applicable to the system under consideration. With some very rough approximations for the dielectric constant of the medium, the values of the degree of ionization computed from a modified Walden product[40] show that ionization of nitric acid in the organic phase takes place to an appreciable extent, but only at the lowest acid concentrations. At higher acid concentrations, about 0·3 M $HNO_3$ in the organic phase, where compound formation between DBP and $HNO_3$ begins, the ionization ceases entirely.

*Effect of inert diluent*

$CCl_4$ was selected as the organic diluent for DBP; since no inert solvent effect[41] has to be taken into account, and since the extent of dimerization in this solvent is very high[20], the uniformity of the ester species was not expected to change appreciably with the initial concentration of DBP. Data for the extraction of nitric acid into various concentrations of DBP are presented in Fig. 10. This type of plot was chosen in order

[35] O. Redlich, *Chem. Rev.* **39**, 333 (1946).
[36] R. J. Gillespie and D. J. Millen, *Quart. Rev. Chem. Soc., Lond.* **2**, 277 (1948).
[37] J. Chédin, S. Feneant and R. Vandoni, *C. R. Acad. Sci., Paris* **226**, 1722 (1948).
[38] J. Chédin, *J. Chem. Phys.* **49**, 109 (1952).
[39] T. Shedlovsky and R. L. Kay, *J. Phys. Chem.* **60**, 151 (1956).
[40] N. G. Foster and E. S. Amis, *Z. Phys. Chem.* **3**, 365 (1955).
[41] D. G. Tuck, *J. Inorg. Nucl. Chem.* **11**, 164 (1959).

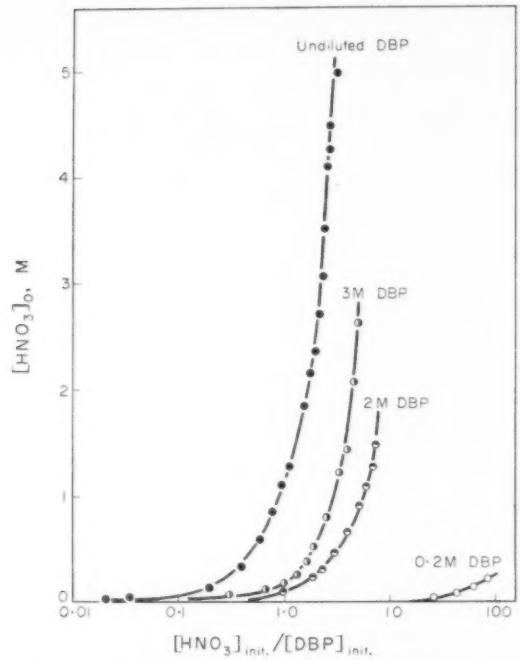



FIG. 10.—Distribution isotherms for nitric acid at various DBP concentration in $CCl_4$ diluent.

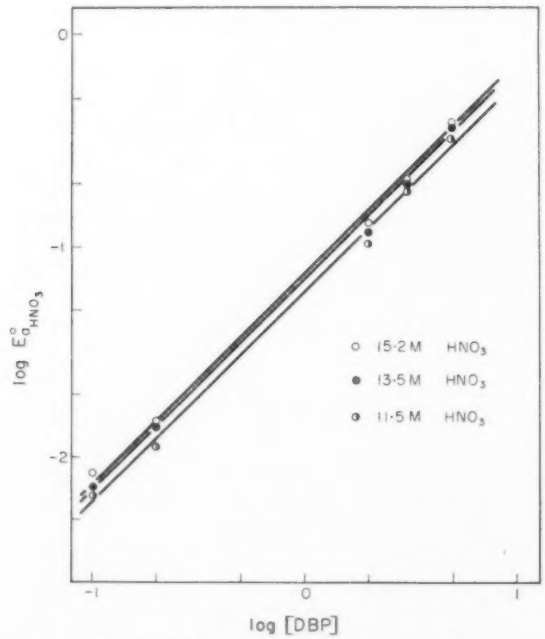



FIG. 11.—The extraction ratio of nitric acid as a function of DBP concentration at various initial nitric acid concentrations.

to show that the interaction of DBP and $HNO_3$ is virtually unaffected by the non-polar solvent $CCl_4$, a phenomenon already observed for similar TBP systems.[29,30]

In view of the existence of several nitric acid solvates in the organic phase in the system under consideration, the extractant–dilution approach for the determination of the solvation number can only be valid at a specific nitric acid concentration either when only one and the same solvate exists, or at least predominates, for all DBP dilutions. Similar phenomena have been noted in systems containing TBP.[33,34,42,43] In the present case only high acid concentrations fulfil the above requirement. From Fig. 11 it may be seen that under the acidity conditions stated, $E^{\circ}_{a_{HNO_3}}$ shows a direct first-power dependence upon the concentration of DBP in the organic phase. The deviations of some points from the first-power law are appreciable, but hardly sufficient to cause us to doubt that it is the true limiting law.

Although the inert solvent in the system under consideration seems to be incapable of effecting the extraction mechanism involved, it is able, however, to influence in many cases the nature of the organic phase. There is evidence in this work to show that its presence inhibits, for example, the ionization of nitric acid in the ester phase.

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*Equilibrium mechanism*

In this system under the experimental conditions employed, the course of nitric acid extraction may be described by the following consecutive reactions:

$$(DBP)_{2org} + 2H_2O_{aq} \longrightarrow (DBP.H_2O)_{2org} \quad (1)$$

$$(DBP.H_2O)_{2org} + HNO_{3aq} \longrightarrow (DBP.H_2O)_2.HNO_{3org} \quad (2)$$

$$(DBP.H_2O)_2.HNO_{3org} + HNO_{3aq} \longrightarrow 2DBP.H_2O.HNO_{3org} \quad (3)$$

$$DBP.H_2O.HNO_{3org} + HNO_{3aq} \longrightarrow DBP.H_2O.(HNO_3)_{2org} \quad (4)$$

When DBP is in contact with water or very dilute aqueous solutions of nitric acid, only the first reaction between water and DBP occurs. The nitric acid extracted under these conditions is appreciably ionized when no diluent is present in the system. The decreasing extraction ratio with increasing initial acid concentrations up to approximately 1 M (Table 1) is explained by ever-decreasing dissociation of the acid in the organic phase. The end of the ionization range, at about 0·1 M organic acidity, and the first break in the physical properties of the organic phase presented in Figs. 4–7 at approximately the same initial nitric acid concentration, are undoubtedly related.

At initial acid concentrations between ~1 M and ~9 M the extraction seems to be entirely due to the interaction between the dimer-dihydrate and the unhydrated nitric acid molecule, according to equation (2). The formation constant

$$K_1 = \frac{[(DBP.H_2O)_2.HNO_3]_{org}}{[(DBP.H_2O)_2]_{org}[HNO_3]_{aq}}$$

where $[HNO_3]_{aq}$ is the concentration of undissociated nitric acid in the equilibrium aqueous phase,[44] was calculated only up to experiment (11) (Table 1), where the $[HNO_3]_0/[DBP]_0$ ratio in the organic phase is 0·5. The values computed are shown

[42] K. Alcock, F. C. Bedford, W. H. Hardwick and H. A. C. McKay, *J. Inorg. Nucl. Chem.* **4**, 100 (1957).
[43] E. Hesford, H. A. C. McKay and D. Scargill, *J. Inorg. Nucl. Chem.* **4**, 321 (1957).
[44] W. J. Hamer (Editor), *The Structure of Electrolytic Solutions*, p. 43. Wiley, New York (1959).

in Table 2. The fact that at the two lowest acid concentrations the acid dependence expressed by the equation for $K_1$ is not truly represented indicates that at these concentrations some other process is taking place. At the above concentrations the nitric acid is ionized in the organic phase. The deviation in the border region (experiment 11) may result from the presence of the next species, or some unidentified intermediate. In view of the fact that concentrations rather than thermodynamic activities were substituted for the different species in the equation for $K_1$, complete agreement was not expected. The average value obtained for $K_1 = 2{\cdot}1$, with a mean

TABLE 2.—VALUES FOR THE APPARENT EQUILIBRIUM CONSTANT $K_1$

| No. of exp.* | Conc. of undiss. $HNO_{3aq}$ | $K_1$ | No. of exp.* | Conc. of undiss. $HNO_{3aq}$ | $K_1$ |
|---|---|---|---|---|---|
| 1 | 0·00033 | 23·10 | 7 | 0·298 | 2·01 |
| 2 | 0·00118 | 9·05 | 8 | 0·508 | 1·79 |
| 3 | 0·0066 | 2·61 | 9 | 0·818 | 1·80 |
| 4 | 0·0196 | 2·56 | 10 | 1·98 | 2·07 |
| 5 | 0·069 | 2·22 | 11 | 2·52 | 16·95 |
| 6 | 0·150 | 2·02 | | | |

* See Table 1.

deviation of $\pm 0{\cdot}2$, suggests that the extracted compound was reasonably formulated from the results of the physical–chemical investigations.

The continuous change in the physical properties of the organic solutions can be explained by a strong interaction between associated nitric acid molecules and the first complex formed, and should be formulated as a bimolecular association as presented in equation (3). According to this equation dissociation of the dimeric ester complex takes place. Although it is impossible to infer from the measurements carried out in this investigation whether the particular species identified in the organic phase remains as a dimer in solution or whether the new species formed is a monomer, the dissociation reaction seems to be strongly supported by the viscosity measurements shown in Fig. 6. The viscosity of the organic phase decreases up to a ratio of $(HNO_3)/[DBP]_0 = 1$, when the compound $DBP.H_2O.HNO_3$ is supposed to be quantitatively formed, and remains constant as this ratio increases.

In experiments where DBP was equilibrated with aqueous nitric acid solutions of ~13·5 M and above, the organic nitric acid content was noted to be higher than the concentration of the ester. On the strength of this it is possible to assume the presence of a compound with an empirical formula $DBP.H_2O.(HNO_3)_2$. Although the existence of such a compound cannot be considered as being established, the very pronounced changes in the physical–chemical data of the organic phase seem also to be indicative of a compound formation. The formation of higher $HNO_3$-compounds also cannot be excluded, since they would appear to follow from the possible coordinating properties of oxygen atoms of the two butoxy-groups.

The respective equilibrium constants for equations (3) and (4), calculated on the assumption of 1:1 and 1:2 compound formation between DBP and $HNO_3$, yielded a scattered set of values. It is clear that at higher acidities the simplified method of calculation, adopted for $K_1$ is inadequate. It does not mean, however, that our

postulate of consecutive higher nitric acid adducts breaks down. Apparently it is impossible to describe adequately the reactions without considering activity factors. It would be unjustifiable to carry out thermodynamic analyses of the equilibria involved without first knowing the activity coefficients of the *molecular compounds* in the organic phase. These may not reasonably be expected to remain constant as the ionic strength of the organic phase changes and consequently complicates the quantitative application of the equations. To solve this problem, an alternative experimental approach is required, involving the use of very dilute solutions, We are mainly concerned, however, with the molecular picture of the organic phase, irrespective of purely thermodynamic considerations.

In conclusion, the difference in the interaction of nitric acid with tri- and di-*n*-butyl phosphate must again be stressed. DBP differs from TBP:

(i) in allowing appreciable ionization of nitric acid at low concentrations,
(ii) in forming hydrated species, and
(iii) in forming a series of different solvates, at least under the experimental conditions outlined in this paper.

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*Note added in proof*—After this paper had been accepted for publication, a report[45] appeared dealing with the extraction of nitric acid by di-*n*-butylphosphoric acid. These results are substantially in agreement with ours.

[45] B. F. GREENFIELD and C. J. HARDY, AERE–R 3686 (March, 1961).

J. Inorg. Nucl. Chem., 1961, Vol. 21, pp. 124 to 132. Pergamon Press Ltd. Printed in Northern Ireland

# ION EXCHANGE PROPERTIES OF ZIRCONYL PHOSPHATES—I

## CONTRIBUTION TO THE STRUCTURE OF ZIRCONYL PHOSPHATES

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**Abstract**—Chemical and X-ray investigations on zirconyl phosphates have led to the elucidation of some aspects of the structure of a crystalline compound with a constant phosphate/zirconium ratio of 5/3. The ion-exchange properties of this compound have been investigated by studying the mode of dissociation and the total exchange capacity. The total capacity amounts to 4·3 ± 0·10 meq/g at pH = 7·5 and the capacity-composition curve indicates that in acid and neutral media the phosphate groups only are responsible for the exchange capacity.

A crystallographic investigation has led to the determination of a cubic structure with parameter $a = 9{\cdot}04$ Å. In conjunction with density measurement it has been possible to calculate the molecular weight of one chain unit (M = 878).

THE first reports on synthetic inorganic absorbents for the treatment of reprocessing solutions were published by RUSSEL *et al.*[1] and by BEATON *et al.*[2] in 1943, but these reports were not declassified until 1957. During the last few years attention has been drawn, principally by KRAUS *et al.*[3,4] and AMPHLETT *et al.*[5–7] to the possibilities of using the synthetic mineral ion exchangers for high-level waste treatment, recovery of fission products and high-temperature ion exchange. These exchangers are unlike the commercial organic exchangers, stable towards intense radiation and high temperature. The most important acid-stable, synthetic mineral ion exchangers which have been investigated recently are on the one hand the very sparingly soluble salts of the heteropoly acids, e.g. some metal salts of phosphotungstic[8] and phosphomolybdic acids[9] and on the other the insoluble salts or oxides of Zr, Ti, Th[3–7,10] and other easily hydrolysable polyvalent cations. The synthetic zeolites,[11] although stable towards radiation and high temperature, are not acid stable and cannot be used for the treatment of acid reprocessing solutions. A comparative study of the ion-exchange properties of Zr, Ti and Th phosphates[5,12] has demonstrated that Zr phosphate seems to be the most promising exchanger, since its capacity proves to be much higher than that of Ti and Th phosphates.

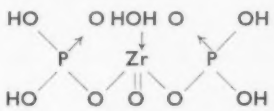
[1] E. R. RUSSEL, A. W. ADAMSON, J. SCHUBERT and G. E. BOYD, U.S.A.E.C. Report CN–508 (1943)
[2] R. H. BEATON *et al.*, U.S.A.E.C. Report CN–633 (1943).
[3] K. A. KRAUS and H. O. PHILLIPS, *J. Amer. Chem. Soc.* **78**, 694 (1956).
[4] K. A. KRAUS, H. O. PHILLIPS, T. A. CARLSON and J. S. JOHNSON, *Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy, Geneva*, 1958. Paper No. 15/P1832 (1958).
[5] C. B. AMPHLETT, *Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy, Geneva*, 1958. Paper nr. 15/P/27 (1958).
[6] C. B. AMPHLETT, L. A. MCDONALD, M. J. REDMAN, *J. Inorg. Nucl. Chem.* **6**, 220 (1958).
[7] C. B. AMPHLETT, L. A. MCDONALD, T. S. BURGESS, J. C. MAYNARD, *J. Inorg. Nucl. Chem.* **10**, 69 (1959).
[8] T. V. HEALY, B. L. DAVIES, AERE/C/R 2528, 2577; A.E.R.E. R 2969.
[9] J. VAN R. SMIT, W. RABB and J. J. JACOBS, *Nucleonics* **17**, No. 9, 116 (1959).
[10] D. J. O'CONNOR, AERE C/M/230.
[11] R. M. BARRER, *Proc. Roy. Soc.* 99 (1958).
[12] Y. GAL and O. GAL, *Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy, Geneva*, 1958. Paper No. 15/P/468 (1958).

The first part of this series is intended to elucidate some aspects of the structure of certain zirconyl phosphates, in order to make possible a quantitative description of the ion exchange processes necessary for various applications. The aqueous chemistry of Zr compounds is complicated by the fact that many different ionic species can be formed starting from one well defined ionic species by hydrolysis and polymerization. A thorough review of the chemistry of Zr has been written by BLUMENTHAL[13], and only some of the basic features of this chemistry will be reviewed here.

One of the best known Zr compounds is the oxychloride $ZrOCl_2 \cdot 8H_2O$; this is readily soluble in water but the chemical identity of the ions in solution changes on standing, and the reaction sequence can be outlined as follows:[14]

$$ZrOCl_2 8H_2O \xrightarrow{H_2O} [Zr_x(OH)_8]^{8+}\ [Cl^- \text{ or } OH^-]_8^{8-} \xrightarrow{H_2O} 4[ZrO(OH)]^+$$

According to JOHNSON and KRAUS[15], $[ZrOOH]^+$ groups polymerize in HCl solution to form trimers and tetramers, the structures of which can be written as $[(ZrO)_3(OH)_3]^+$ and $[(ZrO)_4(OH)_4]^{4+}$; at lower acidities larger aggregates are formed. By adding a zirconyl chloride solution to a solution of ortho phosphoric acid BLUMENTHAL[16] obtained a very insoluble compound, which after washing and drying at 110°C had the composition $ZrO_2 \cdot P_2O_5 \cdot 3H_2O$. This compound behaves in aqueous solution as an acid and its structure can be represented by:




## EXPERIMENTAL

*Preparation of zirconium phosphate* (ZrP)

Several batches (I–VII) with varying phosphate:zirconium ratios (P/Zr) were prepared in the following way: 400 g $ZrOCl_2$ were dissolved in 2 l. of 1 N HCl and filtered to remove suspended material; 500 ml of this solution was added dropwise with vigorous stirring to 1550 ml of solution containing various quantities of concentrated $H_3PO_4$ (in order to obtain different molar ratios of the reacting substances) in 6 N HCl. After the precipitate had settled, the supernatant liquid was filtered and the precipitate washed several times with distilled water. The product was then dried at 50°C to facilitate further washing. It was then washed to pH 3–4 and dried at 50°C.

*Determination of phosphate:zirconium ratios in the product*

The phosphate:zirconium ratio was first obtained by analysis of the supernatant liquid and then by decomposing the ZrP in alkaline solution. Zirconium was determined gravimetrically in the supernatant liquid as $ZrO_2$ after precipitation with $NH_4OH$ and firing at 800°C, and phosphate was determined gravimetrically as $Mg_2P_2O_7$. The results given in Table 1 and plotted in Fig. 1 indicate that the P/Zr ratio in the freshly-settled precipitate is the same as that in the original solution up to a value of 5/3. Above this value the exchanger seems to be nearly saturated with phosphate groups. Indeed, for initial ratios of two and three the ratios in the precipitate are only 1·75 and 1·84. The stoicheiometric ratio two, mentioned by BLUMENTHAL,[16] has not been reached.

By treating the washed ZrP with 0·5 N NaOH the phosphate groups are quantitatively removed by hydrolysis, and the remaining hydrous zirconium oxide can be dissolved in 6 N $NHO_3$. After analysing the NaOH and $HNO_3$ solutions for phosphate and zirconium, it was possible to determine the

[13] W. B. BLUMENTHAL, *The Chemical Behaviour of Zirconium*. Van Nostrand, Princeton (1958).
[14] W. B. BLUMENTAL, *The Chemical Behaviour of Zirconium*, p. 128. Van Nostrand, Princeton (1958).
[15] J. S. JOHNSON and K. A. KRAUS, *J. Amer. Chem. Soc.* **78**, 3937 (1956).
[16] W. B. BLUMENTHAL, *Industr. Engng. Chem.* **46**, 528 (1954).

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TABLE 1.—P/ZR RATIO IN FRESHLY SETTLED ZrP FRACTIONS

| Fraction | I | II | III | IV | V | VI | VII |
|---|---|---|---|---|---|---|---|
| P/Zr ratio of the reacting substances | 3·0 | 2·0 | 1·75 | 1·5 | 1·25 | 1·0 | 0·90 |
| P/Zr ratio in the precipitate | 1·84 | 1·75 | 1·68 | 1·48 | 1·24 | 1·04 | 0·94 |

Phosphate : zirconium ratio in freshly-settled zirconyl phosphates

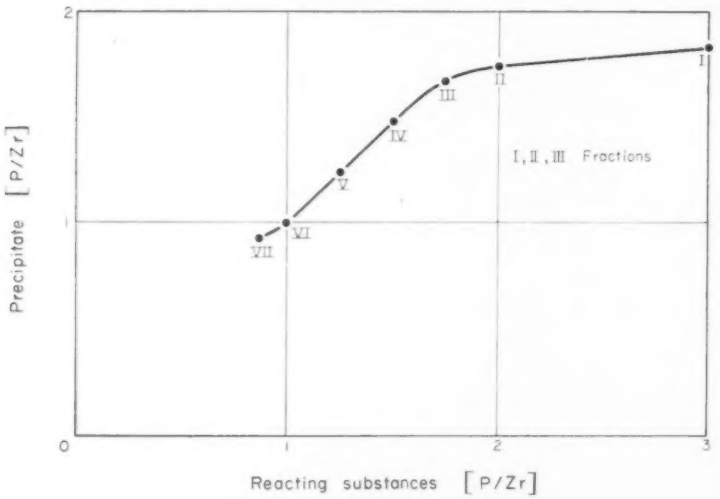


FIG. 1.

P/Zr ratios in the washed precipitates. The results in Table 2 indicate that the excess phosphate groups are removed by washing and that the first three fractions have approximately the same composition. On the other hand one observes the same :-correspondence for the lower-ratio fractions IV, V, VI and VII.

TABLE 2.—P/Zr RATIO IN WASHED ZrP

| Fraction | I | II | III | IV | V | VI | VII |
|---|---|---|---|---|---|---|---|
| P/Zr ratio in solution | 3·0 | 2·0 | 1·75 | 1·5 | 1·25 | 1·0 | 0·90 |
| P/Zr ratio in the washed precipitates | 1·68 | 1·66 | 1·67 | 1·5 | 1·25 | 1·0 | 0·94 |

## DISCUSSION

The experimental results point to the existence of a zirconyl phosphate compound with a constant molar ratio. This ratio can be obtained if there are five phosphate groups per three Zr atoms in the polymer chain. If one takes into account the existence[15] of $[(ZrO)_3(OH)_3]^{3+}$ groups in hydrochloric acid solutions, and assumes that these zirconyl groups react as a whole with the surrounding phosphate groups, a

chain structure can be formed by trimers which are linked by phosphate groups. Experimental support for this postulate is described below. The P/Zr ratio in this structure must attain the value 5/3 or 1·666. . . for an infinite chain length. Each Zr atom of the trimer group is probably surrounded by two phosphate groups. More phosphate groups probably cannot enter the chain unit owing to steric hindrance. The linear increase in the P/Zr ratio in the ZrP fractions IV, V, VI and VII can be explained by a progressive replacement by phosphate of the hydroxyl groups in the hydrous zirconium oxide matrix until the ratio 5/3 has been reached.

*Ion exchange properties of* ZrP

Chemical evidence for this structure can be obtained from a systematic study of the ion-exchange properties of the compounds. The different factors investigated successively, were the hydration, the mode of dissociation of the exchanging groups, the total capacity and the density. The hydration was studied thermogravimetrically with the results shown in Table 3; heating was continued to constant weight.

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TABLE 3.—PER CENT WEIGHT LOSS OF ZrP FRACTIONS OVER DIFFERENT INTERVALS OF TEMPERATURE

| Temp. (°C) | Fraction | | | | | | |
|---|---|---|---|---|---|---|---|
| | I | II | III | IV | V | VI | VII |
| 50–100 | 7·7 | 12·1 | 18·3 | 8·1 | 9·6 | 6·9 | 9·4 |
| 100–400 | 5·7 | 5·74 | 5·80 | 6·32 | 7·4 | 7·1 | 7·75 |
| 400–600 | 2·13 | 2·44 | 2·25 | 1·87 | 1·95 | 1·83 | 1·78 |

The weight loss in the temperature interval 100–400°C is probably due to elimination of coordination water, as it increases with zirconium content. The mean value 5·75 per cent for the first three fractions corresponds to approximately three $H_2O$ molecules per trimer.

The shape of the equilibrium titration curves (Fig. 2) shows that the ZrP's are weakly-acid monobasic cation exchangers with a p$K$ value of approximately three. This value corresponds probably to the p$K$ value of the second hydrogen ion of the activated phosphoric acid group. Closer examination of the titration curves of the fractions V, VI and VII however indicates that these are steeper and that the p$K$ values tend to increase slightly. From these facts one can deduce that

(1) only one hydrogen ion of the $H_2PO_4^-$ group can be exchanged, in acid solution and
(2) the hydroxyl groups of the hydrous zirconium oxide matrix, play a more important part in the phosphate-poor fractions (V, VI, VII).

The available cation exchange capacity of the ZrP fractions is determined by phosphate groups in neutral solution ($5 < pH < 8$). In alkaline solution the phosphate groups are removed by hydrolysis from the hydrous zirconium oxide chain. By using N/10 NaOH it is possible to convert the ZrP into hydrous zirconium oxides, confirming the relationship between the acid salts and hydrous oxides of zirconium postulated by KRAUS[4]. The hydrolysis of the phosphate groups in alkaline solution limits to some extent the possibilities of ZrP as a cation exchanger.

The determination of the total exchange capacity of ZrP in the hydrogen form is complicated by the fact that very large volumes of concentrated reagents are needed in order to obtain an equilibrium between column influent and effluent (equal pH). The exchange rate however can be increased by using buffer solutions to maintain a steep concentration gradient at the solid–liquid interface. The two buffering solutions which have been used were 2 N potassium citrate and 2 N calcium acetate. After attaining equilibrium, the excess solution was washed out and the fixed cation (K or Ca)

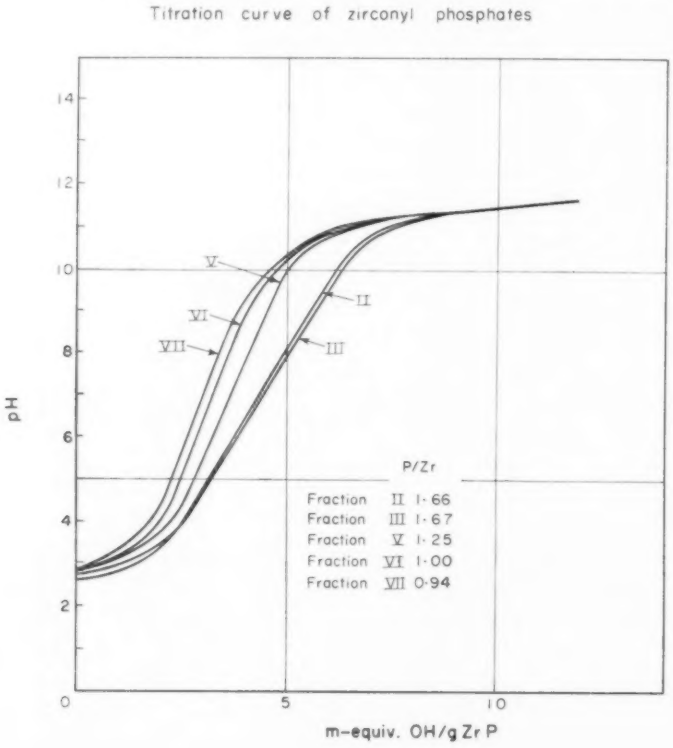


FIG. 2.

eluted with 6 N nitric acid. The results obtained for the different ZrP fractions are presented in Table 4. Different values for the exchange capacity have been mentioned by several authors.[4,6,12] These values depend however upon the saturation method used. With 1 l. of 1 N $Ca(NO_3)_2$ per g of ZrP we obtained a value of 1·88 meq/g which corresponds to the figure given by GAL[12]. If exchange is continued until the pH of influent and effluent are the same much larger volumes are needed. This procedure however is very time-consuming, but can be accelerated considerably by the use of buffer solutions. Examining the results listed in Table 4 and plotted in Fig. 3, one observes three capacity-composition curves with the same slope, indicating that the exchange capacity of fractions I–VI increases in the same way in acid and neutral media. It may be assumed that the capacity in such solutions is due only to phosphate groups. In an alkaline medium, however, the capacity-composition curve is flattened, probably due to the increased cation exchange due to the OH groups in the phosphate-poor fractions.

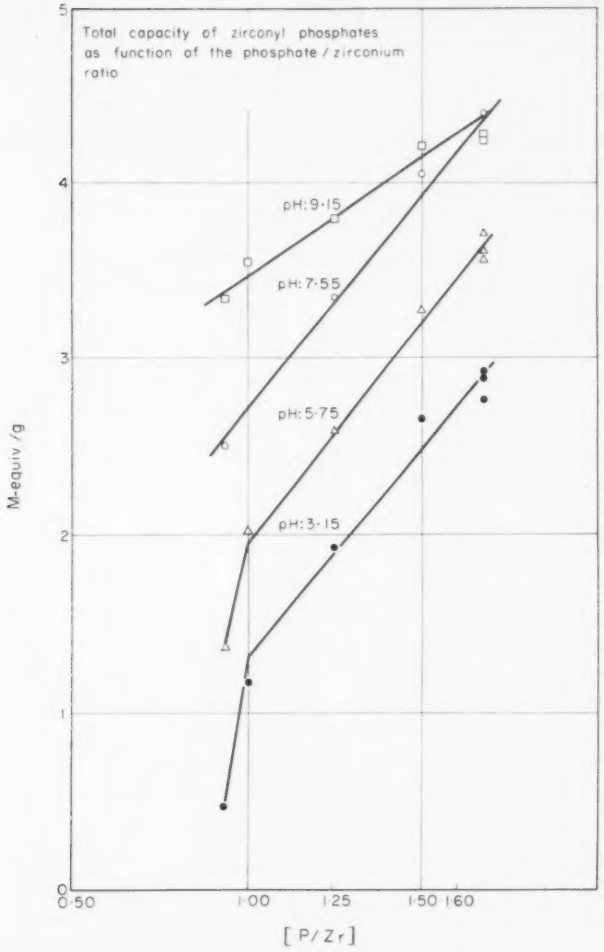


FIG. 3.

TABLE 4.—EXCHANGE CAPACITY IN meq/g OF THE ZrP FRACTIONS AT VARIOUS pH VALUES

| Fraction | pH | | | |
|---|---|---|---|---|
| | 3·15 | 5·75 | 7·55 | 9·15 |
| I | 2·9 | 3·5 | 4·3 | 4·2 |
| II | 2·8 | 3·7 | 4·3 | 4·3 |
| III | 2·9 | 3·6 | 4·4 | — |
| IV | 2·7 | 3·3 | 4·1 | 4·2 |
| V | 1·8 | 2·6 | 3·3 | 3·8 |
| VI | 1·2 | 2·0 | — | 3·5 |
| VII | 0·47 | 1·4 | 2·5 | 3·3 |

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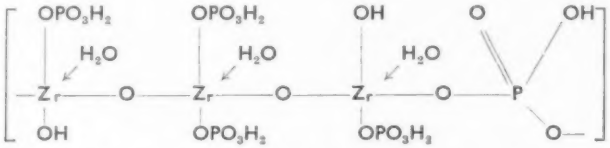
Taking into account the P/Zr ratio of 5/3, the titration characteristics, the hydration and the exchange capacity of 4·3 ± 0·1 meq/g of ZrP. we propose the following structure



The molecular weight of one chain unit is M = 877·6. According to this structure a maximum of four hydrogen ions can be exchanged from the phosphate groups and two hydrogen ions from the hydroxyl groups per chain unit. This would correspond to total theoretical capacities of 4/878 = 4·56 meq/g if only the $H^+$ ions of the phosphate groups could be exchanged, and to 6/878 = 6·84 meq/g if two $H^+$ ions of the hydroxyl groups were exchangeable in addition. The experimental mean value for fractions I, II and III is 4·3 ± 0·1 meq/g, suggesting that only the phosphate groups partake in exchange.

*Physical investigation*

The physical methods used to verify the hypothetical structure based on chemical data were X-ray analysis and density measurements.

*X-ray investigation.* It has previously been reported[6] that ZrP exists as a completely amorphous material. Our chemical investigations however indicated that material with a constant composition could be obtained, and therefore an X-ray study of the material was undertaken. The nearly amorphous structure necessitates the use of a focalization camera with a curved quartz crystal monochromator; copper $K\alpha$ radiation was employed. The results are given in Table 6. A cubic crystal lattice with a unit cell dimension of 9·04 Å can be deduced from the above data for all the fractions except V, which shows a slight deformation of this lattice. An identical crystallographic structure may be attributed to fractions I and III (P/Zr = 5/3), in complete agreement with the results of the chemical investigation. Fraction VI (P/Zr = 1) is characterized by a resolution of the bands into a doublet of intense lines. From the data in Table 6 it can be deduced that the planes of maximum occupation are (100) and (111). The first band with spacing 3·96–3·5 Å can be ascribed to the periodicity of the phosphate groups ($\phi$ = 3·9 Å). The periodicity of the ZrO distances (2·018 Å) can be found in all fractions examined. Further details of symmetry were not determined, since it was impossible to make single crystals.

*Density Measurements.* In conjunction with the X-ray investigation, density

TABLE 5.—DENSITY MEASUREMENTS ON ZrP WITH P/Zr = 5/3

| Displaced liquid | Mol. wt. | Fraction II, Dried at 100°C | Fraction II, Air-dried | |
|---|---|---|---|---|
| | | Degassed | Degassed | Not degassed |
| $CCl_4$ | 158 | 2·30 | — | 2·10 |
| $C_2H_4Br_2$ | 185 | 2·35 | — | 2·11 |
| $H_2O$ | 18 | 2·70 | 2·21 | 2·12 |

measurements were carried out to check the relation between the density and the proposed molecular weight. The measurements were carried out with a pyknometer using several displacing liquids, with the results shown in Table 5. From these data it can be deduced that solvation of the dried ZrP occurs to an extent which is approximately inversely proportional to the molecular weight of the displaced liquid. On the other hand the density of air-dried ZrP which has not been degassed seems to be independent of the solvent used.

TABLE 6.—INTERPLANAR SPACING IN ZrP FRACTIONS (Å)

| Fraction I | | | Fraction III | | | Fraction V | | | Fraction VI | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sharpness | Spacing | *hkl* | Sharpness | Spacing | *hkl* | Sharpness | Spacing | *hkl* | Sharpness | Spacing | *hkl* |
| — | — | | | — | | | — | | $S_w$ | 6·43 | (110) |
| | — | | | — | | | — | | $S_m$ | 5·24 | (111) |
| $S_s$ | 4·50 | (200) | $S_s$ | 4·50 | (200) | $S_s$ | 4·38 | | $B_m$ | 4·36 | |
| | 3·96 | | | | | | | | | 3·97 | |
| $B_s$ | 3·50 | | $B_s$ | 3·49 | | $S$ | 3·21 | (220) | $S_s$ | 3·21 | (220) |
| $S_s$ | 2·63 | (222) | $B_s$ | 2·62 | (222) | $S_s$ | 2·57 | | $S_w$ | 2·60 | (222) |
| $B_w$ | 2·10 | | $B_w$ | 2·08 | | $B_w$ | 2·034 | | $B_w$ | 2·07 | |
| | | | | | | | | | | 1·97 | |
| $S_m$ | 1·70 | (520) | $S_m$ | 1·69 | (520) | $S_m$ | 1·67 | (520) | $B_w$ | 1·68 | |
| | | (432) | | | (432) | | | (432) | | | |
| | — | | | — | | | — | | $S_w$ | 1·58 | |
| $S_w$ | 1·49 | (600) | | — | | | — | | $S_w$ | 1·48 | |

*S* : sharp *B* : band *s* : strong *w* : weak *m* : medium

From the unit cell dimension of 9·04 Å it is possible to calculate either the molecular weight or the crystallographic density, depending on which of these two parameters is known, from the relationship

$$\delta = \frac{M}{a^3 N} \qquad \text{(I)}$$

$\delta$ = density in g cm$^{-3}$
$a$ = unit cell dimension = $9{\cdot}04 \times 10^{-8}$ cm
$M$ = molecular weight of one unit cell
$N$ = Avogadro's number.

Assuming one chain unit with a molecular weight of 878 per unit cell, the density $\delta$ would be 1·95, whereas the measured densities are much higher (Table 5). This may be due to solvation without swelling of the ZrP matrix, resulting in an increased molecular weight. The degree of solvation appears to depend upon the molecular volume of the displaced liquid, since quantitative agreement is found between the density of the solvated product and the molecular weight of the solvent. If we assume a molecular weight of 878 and an uptake of one molecule of $CCl_4$ or $C_2H_4Br_2$ per unit cell, the total molecular weight would be 1036 and 1063 respectively. Using these data in formula I we obtain $\delta(CCl_4) = 2{\cdot}32$ and $\delta(C_2H_4Br_2) = 2{\cdot}36$, corresponding fairly well to the experimental data in Table 5. A quantitative explanation for the very high density of dried ZrP in water has not been found. We may suppose, however, that the pore space in the unit cell can be filled up completely by the small water molecules

(30 Å$^3$) without swelling, but not by the large $CCl_4$ (164 Å$^3$) or $C_2H_4Br_2$ (135 Å$^3$) molecules. On the other hand, the density of air-dried degassed ZrP (fraction II) is 2·21 corresponding to a total molecular weight of 990. Taking into account 12·1% $H_2O$ (Table 3) we may deduce a molecular weight of 866, which is also very near to the postulated value 878. Finally, the fact that water is taken up by ZrP without swelling may also be deduced easily from the increase in the density of the degassed material compared to that which is not degassed.

*Acknowledgements*—The authors wish to thank Dr. M. D'HONT, Dr. N. E. BALLOU and Dr. P. SCHONKEN for the valuable suggestions they offered during the preparation of this manuscript.

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# ION EXCHANGE PROPERTIES OF ZIRCONYL PHOSPHATES—II

## ION EXCHANGE EQUILIBRIA ON ZIRCONYL PHOSPHATE

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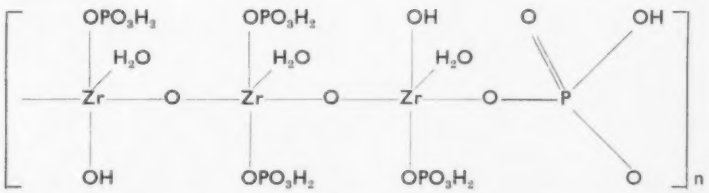
(*Received* 20 *February* 1961)

**Abstract**—The tracer ion exchange equilibria $^{134}Cs$–$H^+$, $^{86}Rb$–$H^+$, $^{89}Sr$–$H^+$, $^{152}Eu$–$H^+$, $^{134}Cs$–$NH_4^+$, $^{89}Sr$–$Na^+$ and $^{89}Sr$–$NH_4^+$ on zirconyl phosphate have been studied in the concentration range 0·001–0·5 M; all obey the mass action law except the $^{89}Sr$–$Na^+$ equilibrium. The distribution coefficients indicate that a selective separation of $^{137}Cs$ from a 0·2 M $HNO_3$ fission product solution can be effected with a very high decontamination factor.

Some macro-exchange systems have been studied in order to evaluate the interference of macro-quantities of cations on zirconyl phosphate in the $H^+$ form. The equilibrium constants of the systems $Na^+$–$H^+$, $K^+$–$H^+$, $Ca^{2+}$–$H^+$ and $Sr^{2+}$–$H^+$ are very low, but the difference between the constants of two neighbouring cations is relatively large.

The adsorption affinity series of the ions in acid solution seems to differ slightly from the lyotropic series, $NH_4^+$ and $H^+$ ions displaying an uncommon behaviour.

RECENT investigation of a zirconyl phosphate(ZrP) with a P/Zr ratio of 5/3[1] suggest the following structure:




Since only one hydrogen ion per $H_2PO_4^-$ group is exchanged at neutral pH, the theoretical capacity is 4·56 meq/g. The experimental exchange capacity, determined by column methods, seemed to be slightly less (4·3 ± 0·1 meq/g), but further investigation by batch methods indicated an exchange capacity of 4·50 ± 0·10 meq/g. This value agrees quite well with the theoretical one and confirms the data given by KRAUS.[2] The latter author[3] and AMPHLETT[4] have studied some ion exchange equilibria on ZrP; both authors mention that the $Cs^+$–$H^+$ and $Ce^{3+}$–$H^+$ equilibria show nearly ideal behaviour, the log $K_d$ curves having slopes of −1 and −3 respectively. By separating Rb and Cs they show the possibility of separating two neighbouring alkali metals on ZrP. The purpose of this report is to contribute to the knowledge concerning tracer equilibria on ZrP in relation to treatment of high level reprocessing waste solutions by ion exchange methods.

[1] L. BAETSLE and J. PELSMAEKERS, *J. Inorg. Nucl. Chem.* **21**, 124 (1961).
[2] K. A. KRAUS, H. O. PHILIPS, T. A. CARLSON, and J. S. JOHNSON *Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy, Geneva* (1958). Paper 15/P/1832 United Nations (1959).
[3] K. A. KRAUS and H. O. PHILLIPS, *J. Amer. Chem. Soc.* **78**, 694 (1956).
[4] C. B. AMPHLETT, L. A. MCDONALD, and J. M. REDMAN *J. Inorg. Nucl. Chem.* **6**, 220 (1958).

## ION EXCHANGE EQUILIBRIA OF TRACER IONS ON ZrP

The tracer ion-exchange equilibria which were investigated on ZrP are related to the separation of Cs from nitric acid fission product solution and of Sr from the neutralized waste solution. The first aqueous waste solution produced in the reprocessing of nuclear fuel elements by the Purex process[5] contains after 10 years cooling three groups of cationic fission products: the Cs group with $^{137}Cs$, $^{134}Cs$ and $^{87}Rb$, the Sr group with $^{90}Sr$, $^{89}Sr$ and $^{137}Ba$, and the rare earth group from Ce to Lu. In order to obtain quantitative data on the separability of Cs and Sr from the other fission products several equilibria have been investigated. The $^{134}Cs$–$H^+$, $^{89}Sr$–$H^+$, and $^{152}Eu$–$H^+$ systems have been studied in relation to the separation of Cs in acid solution and the $^{134}Cs$–$Na^+$, $^{89}Sr$–$Na^+$, $^{134}Cs$–$NH_4^+$ and $^{89}Sr$–$NH_4^+$ systems in

TABLE 1.—DISTRIBUTION COEFFICIENTS ($K_d$) IN $HNO_3$ SOLUTION (0·001 M–0·5 M) AT 20°C

| $HNO_3$, molar | Ionic equilibria | | | |
|---|---|---|---|---|
| | $^{134}Cs$–$H^+$ | $^{86}Rb$–$H^+$ | $^{152}Eu$–$H^+$ | $^{89}Sr$–$H^+$ |
| 0·0015 | 70,000 | — | — | 12,000 |
| 0·005 | 43,000 | — | — | 1500 |
| 0·01 | 30,500 | 21,200 | 22,000 | 600 |
| 0·05 | 11,200 | 4800 | 2000 | 12 |
| 0·1 | 5700 | 2400 | 250 | — |
| 0·2 | 2800 | 1250 | 32<br>49 | — |
| 0·5 | 1150 | 530 | — | — |

relation to the separation of Sr after neutralisation. The distribution coefficients $K_d$ $\left(= \frac{\text{cpm/g}}{\text{cpm/ml}}\right)$ have been determined by batch experiments, in which 0·5 g of vacuum-dried ZrP in the $H^+$ or $Na^+$ form was equilibrated with 100 ml of $HNO_3$ solution with continuous stirring for 24 hours at constant temperature. The distribution coefficients in nitric acid solution are shown in Table 1 and Fig. 1.

The log $K_d$ curves (Fig. 1) are straight lines with slopes of $-1$ for $^{134}Cs$–H, $-2$ for $^{89}Sr$–H, and $-3$ for $^{152}Eu$–H. The latter results confirm the earlier results of KRAUS[3] and AMPHLETT,[4] the equilibria behaving as ideally between certain limits of $HNO_3$ concentration. The upper values of the distribution coefficients generally show a slight decrease relative to the theoretically extrapolated values, and this deviation is so important for $^{152}Eu$ that counting errors cannot provide sufficient explanation. The formation of complex ions of lower valency could perhaps explain the irregularity. Using the mass action constant expression, it is possible to calculate the selectivity constant in the concentration range over which the log $K_d$ curve is linear. For the univalent exchange system $^{134}Cs$–$H^+$, $K = 127$ between the $HNO_3$ concentrations 0·05 and 0·5 M. For the $^{86}Rb$–$H^+$ system $K = 50$ between 0·01 and 0·5 M $HNO_3$. The bi-univalent system $^{89}Sr$–$H^+$ has $K = 1{\cdot}85 \times 10^{-3}$ between the concentration

[5] E. R. IRISH and W. H. REAS, Symposium on the Reprocessing of Irradiated Fuels, Brussels, 20–25 May (1957); TID. 7534, pp. 83–106 (1957).

limits 0·0015 and 0·05 M. Finally, for the tri-univalent system $^{152}Eu$–$H^+$ $K = 2{\cdot}8 \times 10^{-2}$ between 0·05 and 0·25 M $HNO_3$.

The high selectivity for Cs in comparison with the other radionuclides shows that selective separation of $^{137}Cs$ from the $HNO_3$ fission-product solution can easily be

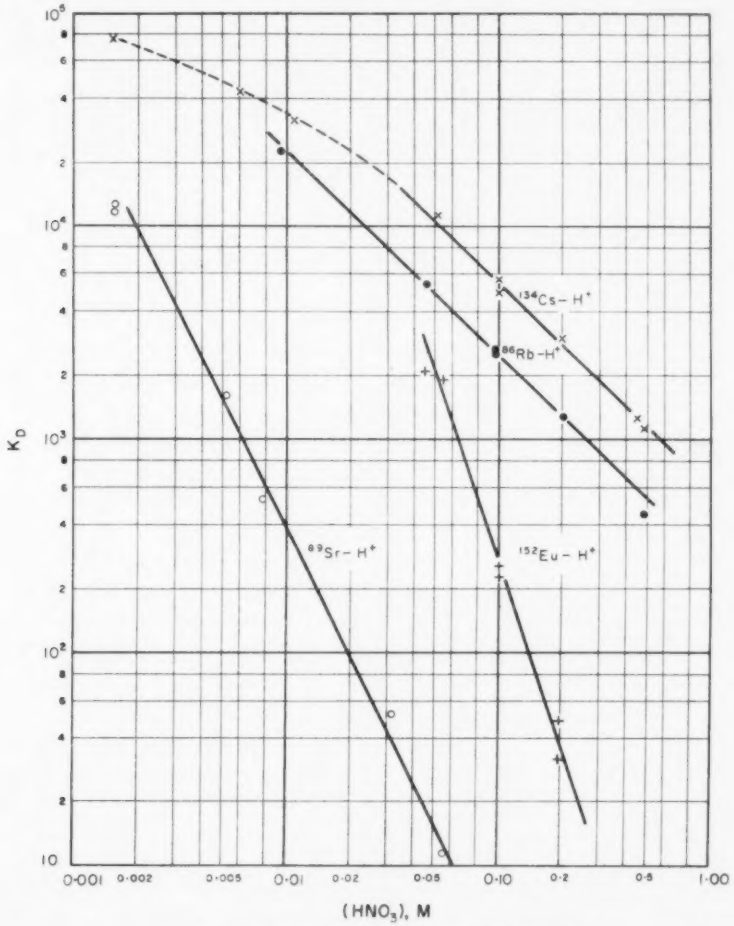



FIG. 1.—Tracer ion exchange equilibria on ZrP.

effected, and cross-contamination by Rb may be neglected. The nitric acid concentration in which this separation can be performed must be selected carefully. Due to the difference in slope between the curves for $^{134}Cs$ and $^{152}Eu$, interference by $^{152}Eu$ (and probably other rare earths) in the selective $^{134}Cs$ removal can be decreased by using $HNO_3$ concentrations $\geq 0{\cdot}2M$. However, the $HNO_3$ concentration should not be higher than 0·5 M because the uptake decreases rapidly above this concentration.[6] Partial deacidification of the fission product solution (1·5 M–5 M $HNO_3$) can be performed by formal treatment[7] or by electrodialysis.[8] Cs recovery from the acid

[6] T. V. HEALY and B. L. DAVIS, AERE/M/451 (1959).
[7] T. F. EVANS, Report HW-58587. (1959).
[8] E. A. MASON and E. J. PARSI, *Proceedings of the Second International Conference for the Peaceful Uses of Atomic Energy, Geneva* (1958). Paper 15/P/502, United Nations (1959).

FP waste solution can be carried out economically if the absorbed Cs can be readily eluted from the ZrP and the latter re-used; this can be achieved using 5 M $HNO_3$.

The exchange properties of ZrP in the $Na^+$ and $NH_4^+$ form have been investigated in order to study the recovery of $^{90}Sr$ from neutralized waste solution. The appropriate distribution coefficients are given in Table 2 and Fig. 2.

The distribution coefficients for Cs and Sr are much higher in $Na^+$ than in $NH_4^+$ solution, and the log $K_d$ curves for the systems $^{134}Cs$–$Na^+$, $^{134}Cs$–$NH_4^+$ and $^{89}Sr$–$NH_4^+$ have the expected theoretical slopes of $-1$ for $^{134}Cs$ and $-2$ for $^{89}Sr$. The mass action constants calculated for these systems are:

$K(Cs–Na) = 98$ between 0·01 and 0·2 M $NaNO_3$

$K(Cs–NH_4) = 3·7$ between 0·005 and 0·2 M $NH_4NO_3$

$K(Sr–NH_4) = 28$ between 0·2 and 0·5 M $NH_4NO_3$

The $^{89}Sr$–$Na^+$ distribution coefficients are much higher than the corresponding $^{134}Cs$–Na distribution coefficients, but the slope of the log $K_d$ curve $-1·65$ does not agree with the theoretically expected value of $-2$. This deviation may be due to unavoidable errors in measurement as the residual activity of the solution in equilibrium with the exchanger was very low. Applying the mass law equation to the data for the systems $^{89}Sr$–Na at 0·5 M $NaNO_3$, one obtains $K(Sr–Na) = 440$; this value is the highest obtained in this investigation. The difference between the behaviour of Sr in acid and neutral media is striking, and may be due to different chemical states of Sr in the two media. In acid solution Sr behaves as a bivalent cation, whereas in neutral solution the formation of $SrOH^+$ with different adsorbability may be assumed.[9] Due to the absence of $Ca^{2+}$, and neglecting the trace of $Ba^{2+}$ in aged waste solutions, one can deduce that an almost selective adsorption of $^{90}Sr$ from neutralized waste solution can be performed, as the rare earths are precipitated in a neutral medium and the anionic nuclides pass through the ZrP column. A quantitative separation of $^{90}Sr$ from the neutralized solution would not be expected, since the precipitate of rare earths and other chemical impurities formed during the neutralization will carry down a small fraction of the $^{90}Sr$.

As has been mentioned by AMPHLETT,[4] the $NH_4^+$ ion has a much higher affinity for ZrP than $Na^+$ ion, and this fact explains the lower values of the distribution coefficients in the $NH_4^+$ solution. However, during the elution of Cs with $NH_4Cl$, two exchange processes occur at the same time: the $NH_4^+$–$H^+$ gross-exchange and the $NH_4^+$–Cs tracer exchange. The transformation of the ZrP–$H^+$ form into the ZrP–$NH_4^+$ form proceeds relatively slowly, so that the volume of eluate containing Cs becomes too large for practical purposes.

## ION EXCHANGE EQUILIBRIA BETWEEN IONS IN MACROSCOPIC CONCENTRATIONS

In order to determine the influence of macroscopic concentrations of several ions on the Cs separation in acid solution the $Na^+$–$H^+$, $K^+$–$H^+$, $Ca^{2+}$–$H^+$ and $Sr^{2+}$–$H^+$ systems were studied. The determination of the equilibrium constants of these systems permits a better understanding of the ion exchange reactions on ZrP. It has

[9] J. VAN R. SMIT, W. ROBB and J. J. JACOBS, *Nucleonics* **17**, 9, 116 (1959).

TABLE 2.—DISTRIBUTION COEFFICIENTS ($K_d$) IN NEUTRAL SOLUTIONS

| $NaNO_3$ or $NH_4NO_3$, molar | $^{134}Cs$–$Na^+$ | $^{134}Cs$–$NH_4^+$ | $^{89}Sr$–$Na^+$ | $^{89}Sr$–$NH_4^+$ |
|---|---|---|---|---|
| 0·01 | 36,000 | 1960 | — | 129,000 |
| 0·05 | 8800 | 340 | — | 72,000 |
| 0·1 | 4400 | 175 | — | 42,000 |
| 0·2 | 2200 | 80 | 110,000 | 14,000 |
| 0·5 | — | — | 36,000 | 2200 |

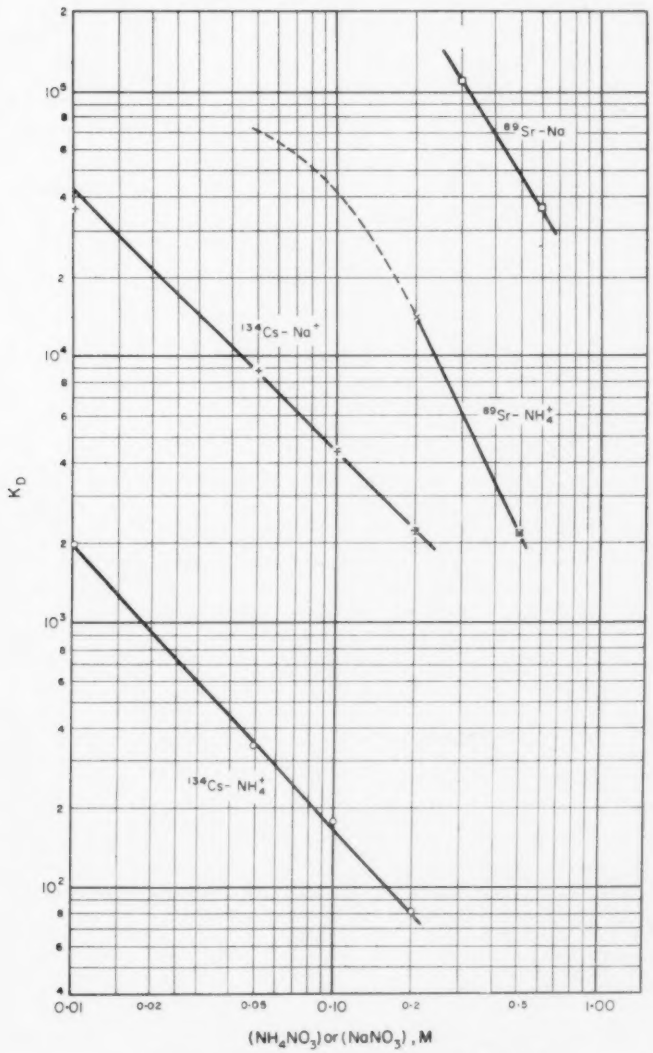



FIG. 2.—Tracer ion exchange equilibria on ZrP.

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been found recently[3,10] that Rb and Cs can be separated on ZrP, due to the large difference in affinity between the two alkali metals.

$$\alpha = \frac{K_{CsH}}{K_{RbH}} = 2{\cdot}5$$

The present investigations provide some information about two other neighbouring pairs of cations, viz. $Na^+$–$K^+$ and $Ca^{2+}$–$Sr^{2+}$.

TABLE 3.—EXPERIMENTAL AND CALCULATED EQUILIBRIUM CONCENTRATIONS OF $Na^+$ AND $H^+$ IN THE ION EXCHANGER AND IN THE SURROUNDING SOLUTION

| | | | | | |
|---|---|---|---|---|---|
| $C_{Na}$ | 0·0102 | 0·0465 | 0·0947 | 0·1977 | 0·4680 |
| $q_{Na}$ | 0·187 | 0·393 | 0·480 | 0·548 | 0·754 |
| | 0·178 | 0·320 | 0·478 | 0·582 | 0·725 |
| $C_H$ | 0·0018 | 0·0039 | 0·0048 | 0·0054 | 0·0075 |
| $q_H$ | 4·31 | 4·11 | 4·02 | 3·96 | 3·75 |
| $q_{el}$ | 0·0052 | 0·0023 | 0·048 | 0·100 | 0·247 |
| $K$ | $9{\cdot}5 \times 10^{-3}$ | $10{\cdot}3 \times 10^{-3}$ | $8{\cdot}8 \times 10^{-3}$ | $7{\cdot}1 \times 10^{-3}$ | $6{\cdot}7 \times 10^{-3}$ |

TABLE 4.—EXPERIMENTAL AND CALCULATED EQUILIBRIUM CONCENTRATIONS OF $K^+$ AND $H^+$ IN THE ION EXCHANGER AND IN THE SURROUNDING SOLUTION

| | | | | | |
|---|---|---|---|---|---|
| $C_K$ | 0·0034 | 0·0283 | 0·0632 | 0·1440 | 0·359 |
| $q_K$ | 0·337 | 0·723 | 0·803 | 0·900 | 1·03 |
| | 0·377 | 0·744 | 0·813 | 0·900 | 1·00 |
| $C_H$ | 0·0035 | 0·0073 | 0·0080 | 0·0090 | 0·0101 |
| $q_H$ | 4·15 | 3·77 | 3·70 | 3·60 | 3·48 |
| $q_{el}$ | 0·0031 | 0·0162 | 0·0272 | 0·0585 | 0·130 |
| $K$ | $8{\cdot}6 \times 10^{-2}$ | $6{\cdot}6 \times 10^{-2}$ | $5{\cdot}5 \times 10^{-2}$ | $2{\cdot}7 \times 10^{-2}$ | $1{\cdot}4 \times 10^{-2}$ |

## EXPERIMENTAL TECHNIQUES

The analytical techniques used in this study were adopted in a slightly simplified form from BAUMANN and ARGERSINGER[11]. An accurately weighed quantity of ZrP was contacted with a salt solution of known concentration for a week, with intermittent stirring; the supernatant solution was then filtered off and the exchanging ions analysed by appropriate methods. The equilibrated ZrP was divided into two approximately equal parts, which were wiped dry with filter paper and weighed immediately. One part was used for elution of the exchanged ions with 6 M $HNO_3$ and the other washed with distilled water to determine the quantity of free electrolyte in the ion exchanger. After drying at 100°C, the water content of the two fractions was deduced from the weight loss. Sodium, potassium and calcium were determined by flame photometry, and strontium by the isotope dilution method; hydrogen ions were titrated potentiometrically.

## RESULTS AND DISCUSSION

The concentrations ($q$) of the ions in the ion exchanger are expressed in meq/g, and the concentration ($c$) of the ions in the solution in meq/ml. The ions in the interstitial spaces of the ion exchanger ($q_{el}$), although not fixed on the material, are also expressed in meq/g. The equilibrium constant $K$ has been calculated from the experimental results using the formula given by BOYD[12]. The results are given in Tables 3–4 for Na, $K$, Ca and Sr respectively.

[10] C. B. AMPHLETT, L. A. MCDONALD, J. S. BURGESS and J. C. MAYNARD, *J. Inorg. Nucl. Chem.* **10**, 269 (1959).
[11] E. W. BAUMANN and W. J. ARGERSINGER, *J. Amer. Chem. Soc.* **78**, 1130 (1956).
[12] G. E. BOYD, J. SCHUBERT and A. W. ADAMSON, *J. Amer. Chem. Soc.* **69**, 2819 (1947).

The equilibrium constants for the few ions investigated relative to $H^+$ on ZrP are very low compared with the known values for synthetic sulphonated ion exchangers. This fact may be ascribed to the weakly acidic nature of the $H_2PO_4^-$ functional groups.

In view of the agreement between the equilibrium constants of the system $Sr^{2+}$–$H^+$ obtained by tracer experiments and by macroscopic exchange at very low solution concentration, we have assumed that both methods lead under these conditions to

TABLE 5.—EXPERIMENTAL AND CALCULATED EQUILIBRIUM CONCENTRATIONS OF $Ca^{2+}$ AND $H^+$ IN THE ION EXCHANGER AND IN THE SURROUNDING SOLUTION

| | | | | | |
|---|---|---|---|---|---|
| $C_{Ca}$ | 0·0066 | 0·0454 | 0·0924 | 0·1900 | 0·4880 |
| $q_{Ca}$ | 0·336 | 0·486 | 0·598 | 0·760 | 0·840 |
| | 0·326 | 0·599 | 0·609 | 0·810 | 0·870 |
| $C_H$ | 0·0033 | 0·0048 | 0·0060 | 0·0070 | 0·0085 |
| $q_H$ | 4·17 | 3·96 | 3·90 | 3·77 | 3·64 |
| $q_{et}$ | 0·0036 | 0·0110 | 0·0304 | 0·0500 | 0·1450 |
| $K$ | $2·1 \times 10^{-4}$ | $2·1 \times 10^{-4}$ | $2·7 \times 10^{-4}$ | $3·8 \times 10^{-4}$ | $4·6 \times 10^{-4}$ |

TABLE 6.—EXPERIMENTAL AND CALCULATED EQUILIBRIUM CONCENTRATIONS OF $Sr^{2+}$ AND $H^+$ IN THE ION EXCHANGER AND IN THE SURROUNDING SOLUTION

| | | | | | |
|---|---|---|---|---|---|
| $C_{Sr}$ | 0·0036 | 0·041 | 0·0895 | 0·1860 | 0·4690 |
| $q_{Sr}$ | 0·645 | 0·913 | 0·970 | 1·24 | 1·60 |
| | 0·595 | 0·803 | 1·03 | 1·16 | 1·90 |
| $C_H$ | 0·0061 | 0·0085 | 0·0100 | 0·0120 | 0·0175 |
| $q_H$ | 3·88 | 3·65 | 3·50 | 3·20 | 2·75 |
| $K$ | $2·5 \times 10^{-3}$ | $1·7 \times 10^{-3}$ | $2·0 \times 10^{-3}$ | $2·4 \times 10^{-3}$ | $4·9 \times 10^{-3}$ |

approximately the same exchange constants. This is equivalent to assuming a solution activity coefficient of unity in both cases. Equilibrium constants obtained by both methods are given in Table 7.

TABLE 7.—EQUILIBRIUM CONSTANTS (EXTRAPOLATED TO ZERO CONCENTRATION FOR THE MACRO-EQUILIBRIA) ON ZrP IN THE $H^+$, $Na^+$ OR $NH_4^+$ FORM

Tracer equilibria

| System | $^{134}Cs$–$H^+$ | $^{86}Rb$–$H^+$ | $^{89}Sr$–$H^+$ | $^{152}Eu$–$H^+$ | $^{134}Cs$–$Na^+$ | $^{89}Sr$–$Na^+$ | $^{134}Cs$–$NH_4^+$ | $^{89}Sr$–$NH_4^+$ |
|---|---|---|---|---|---|---|---|---|
| K | 127 | 50 | $1·85 \times 10^{-3}$ | $2·8 \times 10^{-2}$ | 98 | (440) | 3·7 | 28 |

Macroscopic equilibria

| System | $Na^+$–$H^+$ | $K^+$–$H^+$ | $Ca^{2+}$–$H^+$ | $Sr^{2+}$–$H^+$ |
|---|---|---|---|---|
| K | $1·0 \times 10^{-2}$ | $7·0 \times 10^{-2}$ | $2·0 \times 10^{-4}$ | $1·7 \times 10^{-3}$ |

In acid media a very large difference in affinity is observed between two neighbouring ions, a result which is not generally encountered in the classical organic ion exchangers, and we may reasonably expect that many separations of cations will be possible on ZrP. The specificity of ZrP for Cs compared with the other cations is very high when the exchanger is in the $H^+$ form. In the $Na^+$ and $NH_4^+$ forms the specificity disappears and becomes even lower than for Sr (probably as $SrOH^+$). The behaviour of ZrP in the $Na^+$ and $NH_4^+$ forms recalls the carboxylic ion exchangers, which possess a higher affinity for bivalent than for monovalent ions.

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Whereas in neutral media the lyotropic affinity series may be expected, in acid media there seems to be a shift in the position of the $NH_4^+$ and $H^+$ ions, but a systematic study of all the exchange equilibria including the alkali metals on ZrP in the $H^+$ form will be necessary before final conclusions may be drawn.

The water and electrolyte content of ZrP equilibrated with solutions of varying concentrations have been measured in order to verify the ion exchange theory of GAINES and THOMAS[13] but no conclusive results have been obtained. The measurement technique[11] is still subject to many uncontrolled variables,[14] e.g. the particle size of the ZrP and the moisture content of the material. By operating under the same conditions it is possible to obtain a series of results which agree among themselves, but if one small detail of the measurement technique is altered another series of results different from the first is obtained.

The calculated equilibrium constants in Tables 3–6 are concentration-dependent, and a more appropriate method must be devised before it will be possible to calculate the activity coefficients of the ions in the solid phase and the thermodynamic equilibrium constants.

*Acknowledgements*—The authors wish to express their gratitude to Dr. P. MECHELYNCK of the analytical chemistry service for the many Na, K, Ca and Sr analyses. They acknowledge Dr. P. SCHONKEN for his valuable comments on the report and Dr. P. DEJONGHE for reviewing the manuscript.

[13] G. L. GAINES and H. C. THOMAS, *J. Chem. Phys.* **21**, 714 (1953).
[14] D. H. FREEMAN, *J. Phys. Chem.* **64**, 1048 (1960).

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# AQUEOUS SYSTEMS AT HIGH TEMPERATURE—II

## LIQUID–LIQUID IMMISCIBILITY IN THE SYSTEM $UO_3$–$SO_3$–$N_2O_5$–$H_2O$ ABOVE 300°C*

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**Abstract**—Apparatus suitable for the observation of liquid–liquid immiscibility in solutions sealed in silica tubes is described. Immiscibility temperatures are reported for 0·04, 0·08 and 0·16 molal uranyl solutions in the system $UO_3$–$SO_3$–$N_2O_5$–$H_2O$. A comparison of the effect of nitric and sulphuric acids on the immiscibility temperature of uranyl sulphate solutions on the basis of total added hydrogen ion shows that at low acidity nitric acid produces a greater increase in immiscibility temperature than sulphuric acid and at high acidity sulphuric acid becomes more effective than nitric acid. In solutions containing low concentrations of excess acid, the substitution of nitrate for sulphate raises the immiscibility temperature, but at high acidities the initial substitution lowers the immiscibility temperature. The data seem to indicate that there is an interdependence between acidity and complexing in this system. The data also show that partial substitution of nitrate for sulphate in a sulphate-based aqueous homogeneous reactor fuel at low added acidity may have some advantage in elevating the liquid–liquid immiscibility temperature. Finally, a significant effect of pressure in elevating the immiscibility temperature is reported.

SEVERAL investigators[1] have studied the effect of various cations on the boundary temperature of liquid–liquid immiscibility of uranyl sulphate–sulphuric acid–water solutions but little attention appears to have been devoted to this phenomenon in uranyl solutions containing more than one anion. Existing evidence[1] shows no indication under a saturation vapour-pressure of a tendency toward liquid–liquid immiscibility in the case of uranyl nitrate solutions at temperatures to above 350°. The purpose of this work was to study the effects of nitrate–sulphate mixtures on the conditions required for two liquid phase formation in order to aid in the elucidation of this phenomenon. It was expected that use of nitrate–sulphate mixtures in uranyl solutions at fixed acidity would give higher immiscibility temperatures than is possible with uranyl solutions containing only sulphate. This would enable aqueous homogeneous reactors using sulphate-based fuels to be operated at higher temperatures without separation of a second liquid phase. This paper contains data on liquid–liquid immiscibility boundary temperatures in the system $UO_3$–$SO_3$–$N_2O_5$–$H_2O$ and a description of the equipment used in the study.

## EXPERIMENTAL

*Solutions.* Stock solutions of stoicheiometric $UO_2SO_4$ and $UO_2(NO_3)_2$ were prepared by dissolving $UO_3 \cdot H_2O$, obtained from Mallinckrodt Chemical Company and containing less than 0·01 per cent metallic impurities, in C. p. $H_2SO_4$ and C. p. $HNO_3$ solutions. Two additional stock solutions of $H_2SO_4$

* This paper was presented at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960, and is based upon work performed at Oak Ridge National Laboratory, which is operated by Union Carbide Corporation for the Atomic Energy Commission.

[1] H. F. MCDUFFIE, *Fluid Fuel Reactors* (Edited by J. A. LANE, H. G. MACPHERSON, F. MASLAN), Chap. 3, pp. 85–127. Addison-Wesley, Reading, Mass. (1958).

and $HNO_3$ were prepared . The stock solutions containing uranium were analysed for total anion by acid–base titration after adsorbing uranyl on a cation exchange resin.[2] Uranium was determined by both controlled potential coulometric titration and ignition at 900° to $U_3O_8$. The solutions used for the experiments were prepared by mixing the analysed stock solutions, measured from burettes or pipettes, with the required amount of water. Since concentrations were calculated on a molality basis (moles per kg of $H_2O$), it was necessary to determine the density of the stock solutions as well as their molar concentrations. Molalities of solutes reported in Tables 1, 2, 3 and 4 are accurate to within ±0·5 per cent.

*Apparatus and technique*. Portions of the solutions to be observed at high temperature were sealed in silica capillary tubing approximately 1 mm i.d. and 3 mm o.d. according to a modification of a previously reported procedure.[3] The solution compartments were routinely prepared about half full of solution at room temperature in order to give 60–90 per cent full compartments in the 300–370° range. The solutions were frozen in a dry-ice–trichloroethylene bath before the final sealing to minimize loss of water from the solution during this operation. The capillaries were suspended for observation in a stirred, liquid eutectic mixture of 30 wt. % $LiNO_3$, 14 wt. % $NaNO_3$, and 56 wt. % $KNO_3$ contained in the apparatus shown in Fig. 1. The liquid salt bath was used in preference to the aluminium block furnace type of apparatus[3] employed in a number of earlier investigations because there was less likelihood of temperature gradients in the vicinity of the capillary. The principal advantage of the metal salt-container arrangement shown in Fig. 1, as compared to the all-glass container previously used for this purpose,[4] was the ability of the metal container to retain the fused-salt mixture if and when rupture of capillaries occurred at high temperatures. Safety for the observer when this happened was assured by surrounding the salt container with a wooden container having glass windows shown in Fig. 1. This permitted the use of a comparatively short-focal-length telescope which was more convenient to use than the larger "Baliscope" with a longer focusing distance employed for remote viewing of capillaries in the earlier salt-bath apparatus[4] for safety reasons. A constant amount of heat was supplied by a hot plate beneath the bath and a variable amount was furnished by a bent Inconel-covered Calrod heater immersed in the bath and connected to the 110 V line through a variable transformer. The capillaries were agitated periodically while they were heated or cooled in the bath by means of a "Vibro-Tool" connected to an interval timer in the manner previously described[3,4]

*Precision of measurement*. The temperature of the salt-bath in the immediate vicinity of the capillary tube under investigation was measured by means of an iron–constantan thermocouple and a modified Brown recording potentiometer having a suppressed zero and a full-scale reading of 5·0 mV. The thermocouple was precalibrated against a platinum : platinum–rhodium thermocouple, and the recording potentiometer was checked periodically against a portable potentiometer to observe any drift in calibration. By the use of this arrangement, the instrumental precision was found to be within approximately ± 0·3°, although the precision of the experimental observations was within approximately ± 0·5°. The temperature of phase separation was determined by observing both the appearance and disappearance of the second phase in order to assure complete reversibility of equilibria. In this and similar past investigations, supersaturation in liquid–liquid systems was not observed.

## RESULTS AND DISCUSSION

A comparison was first made of the effect on the liquid–liquid immiscibility temperature resulting from the addition of nitric and sulphuric acids to stoicheiometric uranyl sulphate solutions.* Table 1 includes data on 0·04 molal $UO_2SO_4$ solutions; Table 2, 0·08 molal $UO_2SO_4$ solutions; and Table 3, 0·16 molal $UO_2SO_4$ solutions. The data on $UO_2SO_4$ and $UO_2SO_4$–$H_2SO_4$ solutions are in agreement with the few experimental data obtained previously in this low concentration range.[4] Data derived

* In this paper, terms such as uranyl sulphate, $UO_2SO_4$, sulphate, uranyl, U(VI), $m_{SO_4^{2-}}$, $m_{NO_3^-}$, and $m_{H^+}$ refer to formal concentrations in solution but not necessarily to actual or proposed species designated as, $UO_2^{2+}$, $SO_4^{2}$, $HSO_4^-$, $NO_3^-$, $H^+$, $UO_2(SO_4)_2^{2-}$, and $UO_2(HSO_4)_2$. Prime components of the system are designated as $UO_3$, $SO_3$, $N_2O_5$, and $H_2O$.

[2] H. O. DAY, J. S. GILL, E. V. JONES and W. L. MARSHALL, *Analyt. Chem.* **26**, 611 (1954).
[3] W. L. MARSHALL, H. W. WRIGHT and C. H. SECOY, *J. Chem. Educ.* **31**, 34 (1954).
[4] F. E. CLARK, J. S. GILL, R. SLUSHER and C. H. SECOY, *J. Chem. Engng. Data* **4**, 12 (1959).

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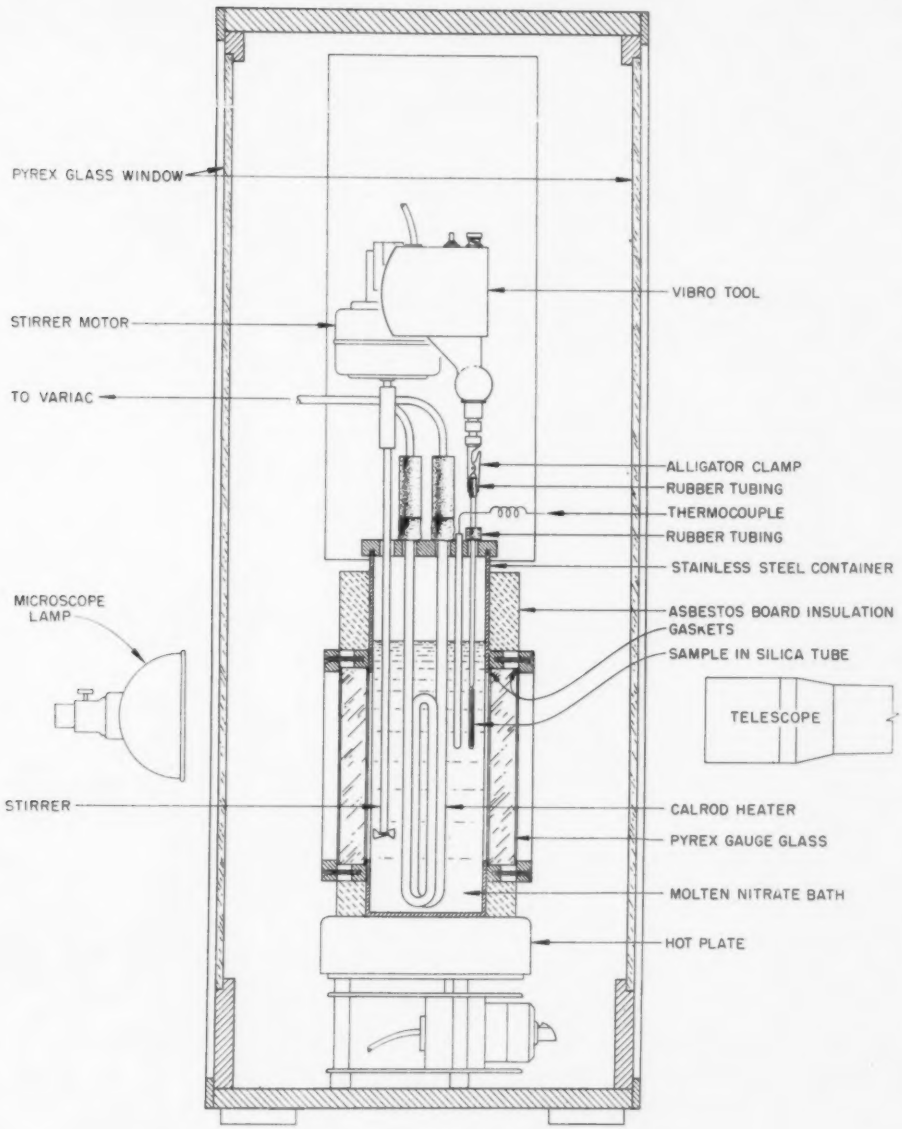


FIG. 1.—Apparatus for determination of phase transitions at elevated temperature and pressure.

from Tables 1, 2 and 3, plotted in Fig. 2, show that the initial addition of nitric acid gives a larger elevation in the two-liquid-phase boundary temperature than $H_2SO_4$ when the two acids are compared on the basis of potentially available $H^+$ added and no transfer of acid to the vapour phase, i.e. one and two gramme atoms of available $H^+$ per mole of added $HNO_3$ and $H_2SO_4$, respectively, present in the liquid phase. Although the second dissociation constant for $H_2SO_4$ is expected to be very small,

based on extrapolation using T. F. YOUNG's equation* to temperatures above 300°, reaction of one mole of $H_2SO_4$ with one mole of $UO_2^{2+}$ ion to produce the $UO_2(SO_4)_2^{2-}$ complex mentioned below would liberate two gramme-atoms of $H^+$.

The $HNO_3$ and $H_2SO_4$ curves for all three U(VI) concentrations show "cross-over" points at temperatures ranging from 353° for 0·04 m U(VI) solutions to 347° for 0·16 m U(VI) solutions when plotted on the above-mentioned basis. The molal ratio, sulphate : uranyl, at the "cross-over" points was found to be relatively constant for

TABLE 1.—LIQUID–LIQUID IMMISCIBILITY TEMPERATURES FOR 0·04 MOLAL URANYL SOLUTIONS; SYSTEM $UO_3$–$SO_3$–$N_2O_5$–$H_2O$

| Total sulphate (*m*) | Total nitrate (*m*) | Immiscibility temp. (°C) | Total sulphate (*m*) | Total nitrate (*m*) | Immiscibility temp. (°C) |
|---|---|---|---|---|---|
| 0·02 | 0·06 | 354* | 0·05 | 0·02 | 341·5 |
| 0·02 | 0·08 | 357 | 0·05 | 0·04 | 346 |
| 0·02 | 0·10 | 359 | 0·05 | 0·08 | 352 |
| 0·02 | 0·14 | 361 | 0·05 | 0·12 | 357 |
| 0·02 | 0·18 | 364 | 0·06 | 0·0 | 340·5 |
| 0·02 | 0·24 | 365 | 0·06 | 0·02 | 345 |
| 0·03 | 0·04 | 342·5* | 0·06 | 0·04 | 348 |
| 0·03 | 0·06 | 349·5 | 0·06 | 0·06 | 350 |
| 0·03 | 0·08 | 352·5 | 0·06 | 0·12 | 357 |
| 0·03 | 0·12 | 356·5 | 0·065 | 0·01 | 344·5 |
| 0·03 | 0·16 | 358 | 0·07 | 0·0 | 347 |
| 0·03 | 0·22 | 364 | 0·07 | 0·04 | 351·5 |
| 0·04 | 0·0 | 328 | 0·07 | 0·08 | 355 |
| 0·04 | 0·01 | 332 | 0·08 | 0·0 | 351 |
| 0·04 | 0·02 | 337 | 0·08 | 0·02 | 352·5 |
| 0·04 | 0·03 | 342 | 0·08 | 0·06 | 355 |
| 0·04 | 0·04 | 344 | 0·08 | 0·12 | 357·5 |
| 0·04 | 0·06 | 350 | 0·09 | 0·04 | 357·5 |
| 0·04 | 0·10 | 354·5 | 0·10 | 0·0 | 358 |
| 0·04 | 0·14 | 357 | 0·10 | 0·08 | 361·5 |
| 0·04 | 0·20 | 362 | 0·11 | 0·0 | 362 |
| 0·05 | 0·0 | 334·5 | 0·12 | 0·04 | 366 |
| | | | 0·14 | 0·0 | 370·5 |

* Some precipitate was observed in the tube before the immiscibility temperature was reached.

the solutions containing no nitrate (2·10, 2·16 and 2·06 for 0·04, 0·08 and 0·16 m U(VI), respectively). If the assumption is made that only one gramme atom of $H^+$ per mole of $H_2SO_4$ is available in solution at the temperatures of interest (300–370°), and, therefore, the addition of one mole of $H_2SO_4$ is compared with one mole of $HNO_3$ then $H_2SO_4$ is more effective than $HNO_3$ in raising the two-liquid-phase temperature. In this case, no "cross-over" points are observed (Fig. 2, dotted curves).

Data derived from Table 1 are plotted in Fig. 3 to show graphically the effect of substituting nitrate for sulphate at different levels of "added acidity," calculated on the assumptions that two gramme-atoms of $H^+$ per mole of $H_2SO_4$ are potentially available, i.e. "added acidity" $= (m_{HNO_3} + 2m_{H_2SO_4})$. Similarly, results derived from Table 2

* Equation reported in LEITZKE and STOUGHTON's paper,[5] and derived by YOUNG for use at much lower temperatures.

[5] M. H. LEITZKE and R. W. STOUGHTON, *J. Amer. Chem. Soc.* **64**, 816 (1960).

TABLE 2.—LIQUID–LIQUID IMMISCIBILITY TEMPERATURES FOR 0·08 MOLAL URANYL SOLUTIONS; SYSTEM $UO_3$–$SO_3$–$N_2O_5$–$H_2O$

| Total sulphate (*m*) | Total nitrate (*m*) | Immiscibility temp. (°C) | Total sulphate (*m*) | Total nitrate (*m*) | Immiscibility temp. (°C) |
|---|---|---|---|---|---|
| 0·04 | 0·10 | 343·5* | 0·08 | 0·32 | 356·5 |
| 0·04 | 0·12 | 346* | 0·09 | 0·0 | 318 |
| 0·04 | 0·16 | 350 | 0·10 | 0·0 | 324 |
| 0·04 | 0·20 | 356 | 0·10 | 0·04 | 335 |
| 0·04 | 0·28 | 361 | 0·10 | 0·08 | 341 |
| 0·06 | 0·06 | 329 | 0·10 | 0·16 | 348.5 |
| 0·06 | 0·08 | 336 | 0·12 | 0·0 | 333 |
| 0·06 | 0·12 | 343 | 0·12 | 0·04 | 341 |
| 0·06 | 0·16 | 348·5 | 0·12 | 0·08 | 344 |
| 0·06 | 0·24 | 353 | 0·12 | 0·12 | 348 |
| 0·08 | 0·0 | 312 | 0·12 | 0·24 | 354 |
| 0·08 | 0·02 | 322 | 0·14 | 0·0 | 340 |
| 0·08 | 0·04 | 330 | 0·16 | 0·0 | 346 |
| 0·08 | 0·08 | 338 | 0·16 | 0·16 | 355 |
| 0·08 | 0·12 | 344 | 0·18 | 0·0 | 352 |
| 0·08 | 0·16 | 347·5 | 0·20 | 0·08 | 360 |
| 0·08 | 0·20 | 351 | 0·205 | 0·0 | 358 |
| 0·08 | 0·25 | 355 | 0·24 | 0·0 | 366·5 |

* Some precipitate was observed in the tube before the immiscibility temperature was reached.

TABLE 3.—LIQUID–LIQUID IMMISCIBILITY TEMPERATURES FOR 0·16 MOLAL URANYL SOLUTIONS; SYSTEM $UO_3$–$SO_3$–$N_2O_5$–$H_2O$

| Total sulphate (*m*) | Total nitrate (*m*) | Immiscibility temp. (°C) | Total sulphate (*m*) | Total nitrate (*m*) | Immiscibility temp. (°C) |
|---|---|---|---|---|---|
| 0·04 | 0·28 | * | 0·16 | 0·32 | 346 |
| 0·04 | 0·40 | 364 | 0·16 | 0·40 | 350 |
| 0·04 | 0·56 | 370·5 | 0·16 | 0·48 | 353 |
| 0·08 | 0·16 | 332·5* | 0·18 | 0·0 | 309 |
| 0·08 | 0·20 | 338* | 0·18 | 0·20 | 338 |
| 0·08 | 0·24 | 345 | 0·20 | 0·0 | 315 |
| 0·08 | 0·32 | 350·5 | 0·20 | 0·24 | 344 |
| 0·08 | 0·40 | 354·5 | 0·21 | 0·14 | 337 |
| 0·12 | 0·08 | 316·5 | 0·24 | 0·0 | 326 |
| 0·12 | 0·12 | 324 | 0·24 | 0·08 | 335 |
| 0·12 | 0·16 | 331 | 0·24 | 0·16 | 341·5 |
| 0·12 | 0·24 | 339 | 0·24 | 0·32 | 350·5 |
| 0·12 | 0·32 | 347 | 0·26 | 0·12 | 341 |
| 0·12 | 0·40 | 351 | 0·28 | 0·0 | 336 |
| 0·16 | 0·0 | 300 | 0·28 | 0·24 | 351·5 |
| 0·16 | 0·04 | 313·5 | 0·32 | 0·0 | 344·5 |
| 0·16 | 0·08 | 322·5 | 0·34 | 0·12 | 354·5 |
| 0·16 | 0·16 | 334 | 0·36 | 0·0 | 354 |
| 0·16 | 0·24 | 340 | | | |

* Some precipitate was observed in the tube before the immiscibility temperature was reached.



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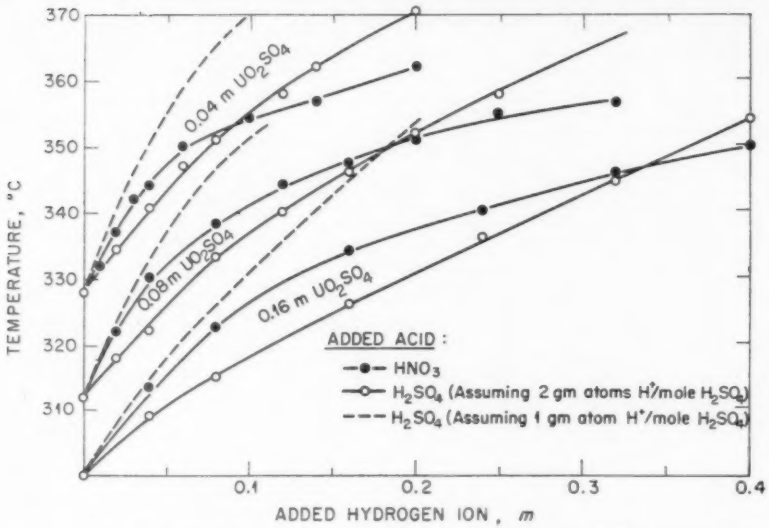


FIG. 2—Effect of $HNO_3$ and $H_2SO_4$ on liquid–liquid immiscibility temperature of $UO_2SO_4$ solutions.

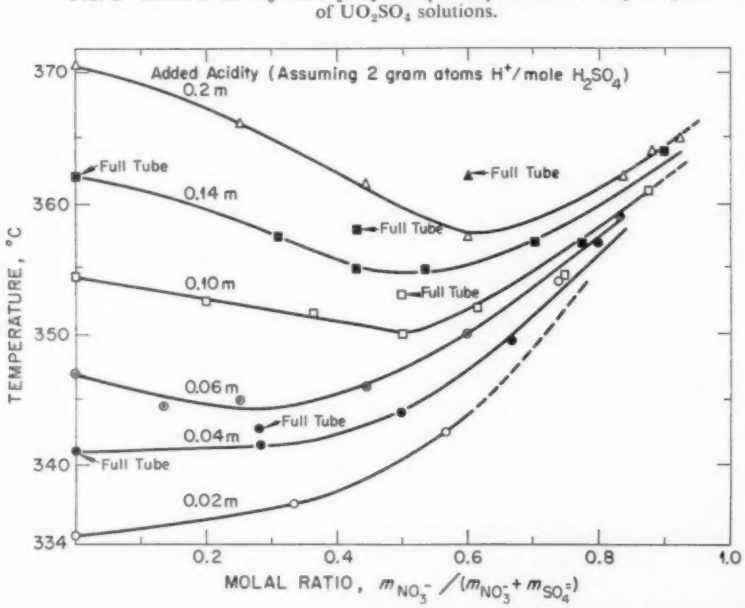


FIG. 3.—Temperature of separation of heavy liquid phase from 0·04 molal U(VI) solutions as a function of acidity and molal ratio $m_{NO_3^-}/m_{NO_3^-} + m_{SO_4^{2-}}$).

are shown in Fig. 4 and those from Table 3 are displayed in Fig. 5. It is apparent that the substitution of nitrate for sulphate at constant "added acidity" raises the liquid–liquid immiscibility temperature of solutions containing low "added acidities" but at higher acid concentrations, on increasing the molal ratio, $m_{NO_3^-}/(m_{SO_4^{2-}})$, the immiscibility temperature goes through a minimum.

Data contained in Table 3 were employed to determine the effect of substituting

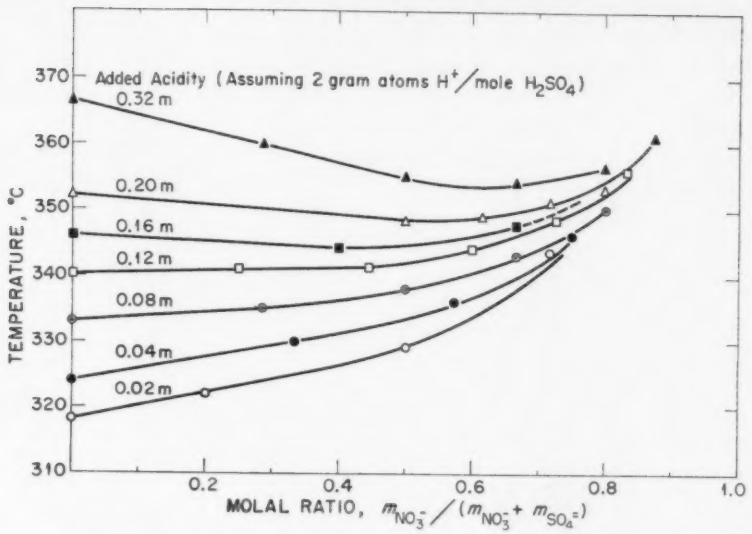


FIG. 4.—Temperature of separation of heavy liquid phase from 0·08 molal U(VI) solutions as a function of acidity and molal ratio, $m_{NO_3^-}/(m_{NO_3^-} + m_{SO_4^{2-}})$.

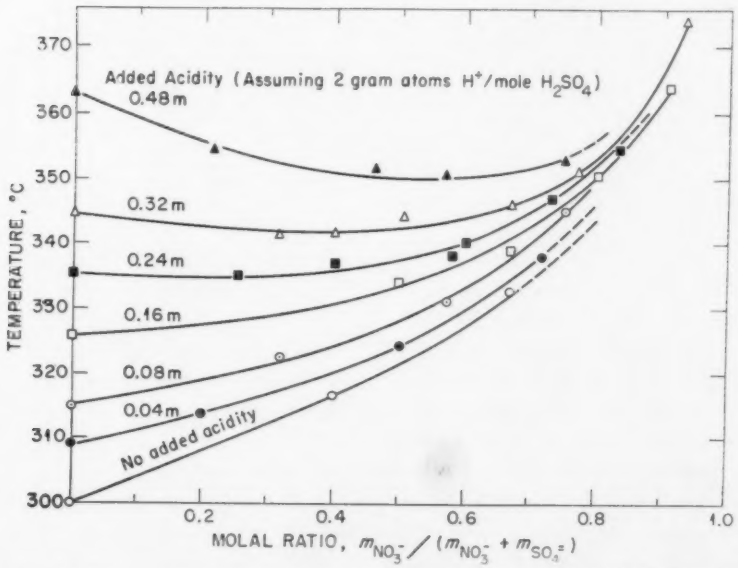


FIG. 5.—Temperature of separation of heavy-liquid phase from 0·16 molal U(VI) solutions as a function of acidity and molal ratio, $m_{NO_3^-}/(m_{NO_3^-} + m_{SO_4^{2-}})$.

nitrate for sulphate at constant "added acidity" calculated on the assumption that the $HSO_4^-$ ion does not dissociate nor does it react with $UO_2SO_4$ to produce $UO_2(SO_4)_2^{2-} + H^+$ at the temperatures of interest. The resulting curves are displayed in Fig. 6 and they show a larger decrease in immiscibility temperature on substituting nitrate ions for sulphate at high concentrations of "added acidity" than do the corresponding curves in Fig. 5.

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Since the immiscibility temperature increases with increasing acidity (Fig. 2), it was thought that this decrease in temperature upon substitution of nitrate for sulphate might be due entirely to nitrate transferring from the liquid to the vapour phase at higher temperatures, thus reducing the concentration of "added acid" in solution. A red-brown coloration of the vapour phase (presumably $NO_2$ gas) was observed with solutions 0·2 m in nitrate or more at temperatures above approximately 340°. In order

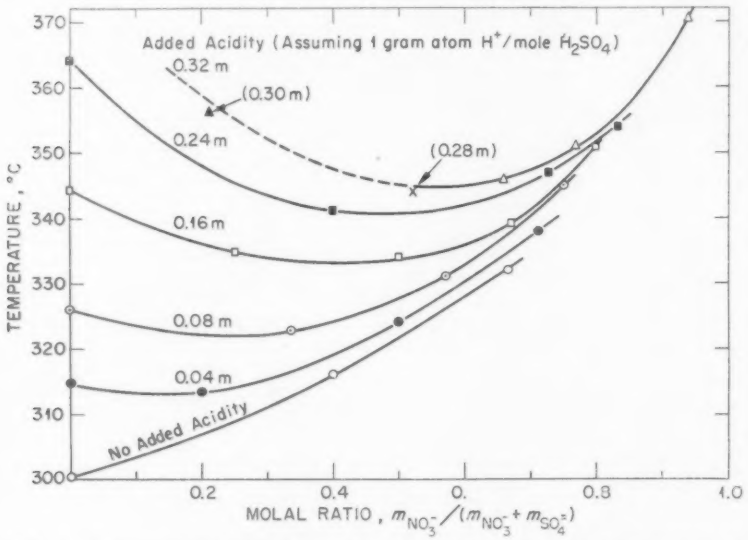


FIG. 6.—Temperature of separation of heavy-liquid phase from 0·16 molal U(VI) solutions as a function of acidity and molal ratio, $m_{NO_3^-}/(m_{NO_3^-} + m_{SO_4^{=}})$; modified added acidity.

to determine the magnitude of the errors that resulted from the transfer of nitrate or sulphate to the vapour phase, immiscibility temperatures were determined for several 0·04 m U(VI) solutions as a function of the volume of sample container filled with liquid at the immiscibility temperature. The data obtained are contained in Table 4 and plotted in Fig. 7. Since there appears to be an approximately linear relationship between immiscibility temperature and volume fraction of liquid in the tube at the separation temperature, at least in the range 40–99 per cent full, extrapolation of the lines to zero vapour volume (100 per cent full) should give reliable values for immiscibility temperatures in the absence of a vapour phase but at saturation vapour-pressures. Comparison of the slopes of the lines obtained with nitrate-containing solutions with those obtained with solutions containing only sulphate (Fig. 7) indicates that some nitrate is going into the vapour phase in the temperature range 336–360°, but the slopes of the lines are surprisingly constant within this temperature range. The extrapolated values shown in Fig. 3 (points marked "full tube") indicate that the dip in the curves at higher acidities is reduced but not removed by eliminating the vapour phase. As a first approximation, the immiscibility temperatures given in Tables 1–3 should be corrected by +1° for solutions containing only sulphate anions to +4° for solutions with moderately high nitrate:sulphate molal ratios in order to obtain full-tube immiscibility temperatures. It would be very desirable to correct all of

the immiscibility data in the manner indicated by Fig. 7 but time was not available to obtain the large amount of additional data required to apply a precise correction of this type for volume filling. It is the opinion of the authors that it is best to report the actual data obtained rather than to apply approximate corrections based on presently

TABLE 4.—VARIATION OF IMMISCIBILITY TEMPERATURE OF 0·04 MOLAL URANYL SOLUTIONS WITH VOLUME PER CENT OF LIQUID IN SAMPLE CONTAINER; SYSTEM $UO_3$–$SO_3$–$N_2O_5$–$H_2O$

| Total sulphate (*m*) | Total nitrate (*m*) | Per cent filled at 25°C | Per cent filled at immiscibility temp. | Immiscibility temp. (°C) |
|---|---|---|---|---|
| 0·05 | 0·02 | 21 | 25 | 336·5 |
| 0·05 | 0·02 | 25 | 31 | 337 |
| 0·05 | 0·02 | 35 | 45 | 338·5 |
| 0·05 | 0·02 | 49 | 71 | 341·5 |
| 0·05 | 0·02 | — | 78 | 341 |
| 0·05 | 0·02 | 60 | 97 | 342·5 |
| 0·06 | 0·0 | 23 | 25 | 336·5 |
| 0·06 | 0·0 | 26 | 31 | 338 |
| 0·06 | 0·0 | 36 | 52 | 339 |
| 0·06 | 0·0 | 51 | 80 | 340 |
| 0·06 | 0·0 | 58 | 98 | 340·5 |
| 0·06 | 0·06 | — | 18 | 342 |
| 0·06 | 0·06 | — | 29 | 346 |
| 0·06 | 0·06 | — | 43 | 348 |
| 0·06 | 0·06 | — | 70 | 350 |
| 0·06 | 0·06 | — | 90 | 352 |
| 0·06 | 0·06 | 56 | 97 | 352 |
| 0·08 | 0·06 | 20 | 18 | 350 |
| 0·08 | 0·06 | 27 | 32 | 353 |
| 0·08 | 0·06 | 39 | 58 | 355 |
| 0·08 | 0·06 | 45 | 73 | 356·3 |
| 0·08 | 0·06 | 53 | 93 | 357 |
| 0·08 | 0·12 | — | 8 | 349 |
| 0·08 | 0·12 | — | 9 | 354 |
| 0·08 | 0·12 | — | 24 | 356·5 |
| 0·08 | 0·12 | — | 47 | 358·5 |
| 0·08 | 0·12 | — | 51 | 358·5 |
| 0·08 | 0·12 | — | 79 | 360·5 |
| 0·08 | 0·12 | — | 99 | 362 |
| 0·11 | 0·0 | 20 | 20 | 361·3 |
| 0·11 | 0·0 | 27 | 31 | 358·9 |
| 0·11 | 0·0 | 29 | 33 | 358·9 |
| 0·11 | 0·0 | 46 | 78 | 361·6 |
| 0·11 | 0·0 | 53 | 98 | 361·8 |

available information. The regularity of experimental data in Figs. 2–6 indicates that deviations in results due to experimental differences in per cent filling of the tubes are probably small.

Figs. 3–5 show that there is some advantage at low "added acidities" in partially substituting nitrate for sulphate to elevate the two-liquid-phase boundary temperature. This information may be of value in selecting sulphate-based aqueous homogeneous reactor fuel compositions.

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From the information in Figs. 3, 4 and 5, it was determined that a molal ratio, sulphate : uranyl, for solutions showing no change in immiscibility temperature on the initial substitution of nitrate for sulphate, i.e.

$$\left(\frac{dt}{dR}\right)_{R\to 0} = 0$$

$$\text{where } R = \frac{m_{NO_3^-}}{m_{NO_3^-} + m_{SO_4^=}}$$

$$t = t^\circ\text{C},$$

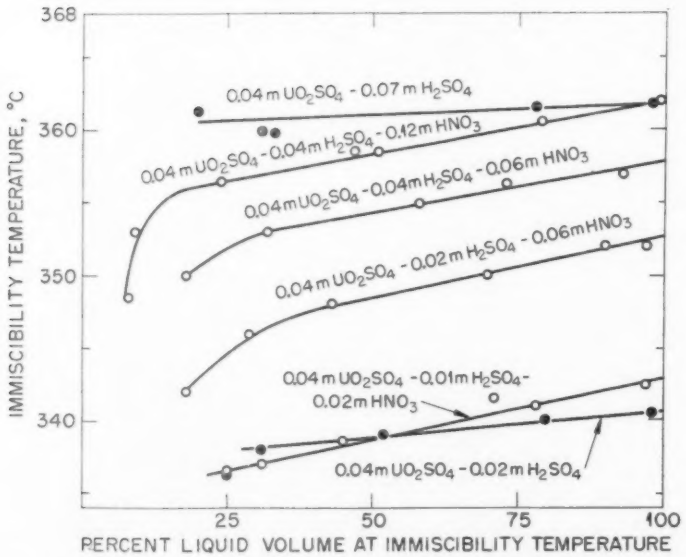
368
360
350
340
IMMISCIBILITY TEMPERATURE, °C
0.04 m UO2SO4 - 0.07 m H2SO4
0.04 m UO2SO4 - 0.04 m H2SO4 - 0.12 m HNO3
0.04 m UO2SO4 - 0.04 m H2SO4 - 0.06 m HNO3
0.04 m UO2SO4 - 0.02 m H2SO4 - 0.06 m HNO3
0.04 m UO2SO4 - 0.01 m H2SO4 -
0.02 m HNO3
0.04 m UO2SO4 - 0.02 m H2SO4
25
50
75
100
PERCENT LIQUID VOLUME AT IMMISCIBILITY TEMPERATURE

FIG. 7.—Variation of immiscibility temperature with volume per cent of liquid in sample container.

is approximately 1·55 for 0·04 m U(VI) solutions (344°), 1·87 for 0·08 m solutions (342°) and 1·75 for 0·16 m solutions (336°). If, however, corrections of the data are made for loss of $HNO_3$ to the vapour phase, as mentioned above, the temperature at which $(dt/dR)_{R\to 0} = 0$ will be higher, and accordingly the amount of "added acidity" for this condition to be satisfied will be greater. Upon examination of data obtained from full-tube experiments (Fig. 3), there may be reason to suspect that the molal ratio, sulphate:uranyl, is near two at the full-tube immiscibility temperature when $(dt/dR)_{R\to 0}$ is 0.

This observation and also the observation on the "cross-over" points (Fig. 2), where the molal ratios, sulphate:uranyl, are approximately two, may indicate complexes such as $UO_2(SO_4)_2^{2-}$ or $UO_2(HSO_4)_2$. This proposition is not unreasonable since investigations[6] of sulphate–bisulphate equilibria to 50° have indicated an increase in the predominant concentration of the bisulphate species as the temperature increases and studies of $UO_2SO_4$ solutions at temperatures up to 200° have already

[6] T. F. YOUNG, L. F. MARANVILLE and H. M. SMITH, *The Structure of Electrolytic Solutions*, Edited by W. J. HAMER, Chap. 4, pp. 35–63. Wiley, New York (1959).

indicated $UO_2(SO_4)_2^{2-}$[5] found previously at lower temperature.[7] The data of GREELEY *et al.*,[8] which show that the addition of $Li_2SO_4$ to aqueous solutions of $UO_2SO_4$ raises the immiscibility temperature until a sulphate : uranyl molal ratio of two is reached, indicates that an important factor in raising the immiscibility temperature in this system may be the formation of the $UO_2(SO_4)_2^{2-}$ or $UO_2(HSO_4)_2$ complex.

An interdependent relationship between acidity and complexing is indicated by the data reported here. For example, the dissociation constant for $HNO_3$ in $H_2O$ solution would appear to decrease sharply as the temperature rises above 300°. This may follow from the equation of YOUNG *et al.*,

$$\log K = 6{\cdot}55_7 - \frac{320{\cdot}88}{T} - 0{\cdot}01359T$$

for the dissociation constant of $HNO_3$ to 306°.[6] The dissociation constant for $HNO_3$ may well be considerably lower than the first dissociation constant for $H_2SO_4$ at the same temperature. For solutions in which the molal ratio, sulphate : uranyl, is low, substitution of a molal amount of $HNO_3$ for either an equivalent or a molal amount of $H_2SO_4$, on the basis of decreasing the free $H^+$ concentration alone, should result in a decreased solubility of heavy-liquid phase. Instead, the solubility is increased; thus, the temperature of formation of two liquid phases is raised as sulphate complexes are replaced by nitrate species which do not promote liquid–liquid immiscibility. At high molal ratios the predominant uranyl species may be $UO_2(HSO_4)_2$ *or* $UO_2(SO_4)_2^{2-}$, which may exhibit some degree of dissociation. Under these conditions the decrease in $H^+$ ion concentration upon the initial substitution of $HNO_3$ for $H_2SO_4$ may be effective in converting $UO_2(HSO_4)_2$ or $UO_2(SO_4)_2^{2-}$ to $UO_2SO_4$, which exhibits a lower solubility in the light-liquid phase. Therefore, the temperature of formation of the second liquid phase decreases. As additional nitrate is substituted for sulphate, the sulphate complexes in the light-liquid phase may be replaced to a large extent by nitrate species and the net effect is an elevation in the immiscibility temperature. Additional information is needed to fully establish this interdependent relationship.

*Significant effect of hydrostatic pressure.* An interesting observation made during the course of the volume-filling experiments was that a solution containing 0·04 m $UO_2SO_4$–0·02 m $H_2SO_4$–0·06 m $HNO_3$ ("full-tube" immiscibility temperature = 352·6°) did not show a phase separation at temperatures up to 360°, the maximum temperature to which it was heated, in a tube that was completely full at 351·5°. This indicates that the immiscibility temperature may be raised significantly by the application of high pressure.

[7] K. A. KRAUS and F. NELSON, *The Structure of Electrolytic Solutions*, Edited by W. J. HAMER, Chap. 23, p. 348. Wiley, New York (1959).
[8] R. S. GREELEY, S. R. BUXTON and J. C. GRIESS, Paper presented at American Nuclear Society Meeting, New York City (1957).

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J. Inorg. Nucl. Chem., 1961, Vol. 21, pp. 152 to 168. Pergamon Press Ltd. Printed in Northern Ireland

# SOLVENT EXTRACTION OF ACTINIDES AND LANTHANIDES FROM MOLTEN SALTS*

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**Abstract**—For the first time, quantitative measurements have been made of distribution coefficients of metal ions between a fused salt phase and an organic phase. The measurements were made at a temperature of 150°C using a $LiNO_3$–$KNO_3$ eutectic (m.p. 120°C) and tributyl phosphate (TBP) as the active extractant with a mixture of polyphenyls as the inert diluent.

Distribution coefficients were determined for Co(II), Eu(III), Nd(III), Am(III), Cm(III), Np(V), Np(VI) and U(VI), and found to be higher by a factor of $\sim 10^2$–$10^3$ as compared with concentrated aqueous nitrate solutions. The number of TBP molecules associated with the complexes $M(NO_3)_p \cdot (TBP)_q$ in the organic phase were found to be the same [except for Co(II)] as those reported for aqueous nitrate system. The effect of $Cl^-$ addition to the nitrate melt was to lower the distribution coefficients.

The separation factor 3·2 for Am(III)/Cm(III) suggests a possible application to the separation of these two elements.

BECAUSE of its great selectivity, solvent extraction has become important as a separation technique. In aqueous systems it has been shown that the presence of salting out agents considerably increases the distribution coefficient of metal ions. In the case of molten salts, the "salting out" process is carried to completion, and very large distribution coefficients from such media were expected. It appeared that a study of solvent extraction from a fused salt solution would yield data which might give a better understanding of the process and possibly lead to some practical applications. Of particular interest was the possibility that separations might be effected which would yield actinide and lanthanide elements in a pure form.

Preliminary experiments had shown[1] that a number of transition metal ions such as Fe(III), Co(II), Ni(II), U(VI), Pr(III) and Nd(III) were extracted essentially quantitatively into pure TBP from molten $LiNO_3$–$KNO_3$ eutectic at 150°C. However no distribution coefficients were measured. Distribution coefficients have now been determined for several actinide and lanthanide elements as a function of the concentration of TBP in the organic phase. In addition, the influence of complexing ions (e.g. $Cl^-$) in the fused salt phase on the distribution coefficients was also studied. To test the dependence of distribution coefficient on oxidation state, Co(II) was studied in addition to the (III), (IV), (V) and (VI) states of various lanthanide and actinide ions.

Because the majority of organic solvents commonly used in extraction processes are unstable at high temperature, it was desirable to work with a salt phase which is liquid at relatively low temperatures. Furthermore, in order to minimize the extraction of metal ions comprising the bulk of the salt phase, alkali metal salts were to be preferred over alkaline earth salts. A suitable compromise was found in the lithium nitrate–potassium nitrate system whose phase diagram has been studied by HARKINS

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.
† On leave of absence from the C.E.N., Mol-Donk, Belgium.

[1] D. M. GRUEN, S. FRIED, P. GRAF and R. L. MCBETH, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, Vol. 8, p. 940. United Nations (1958).

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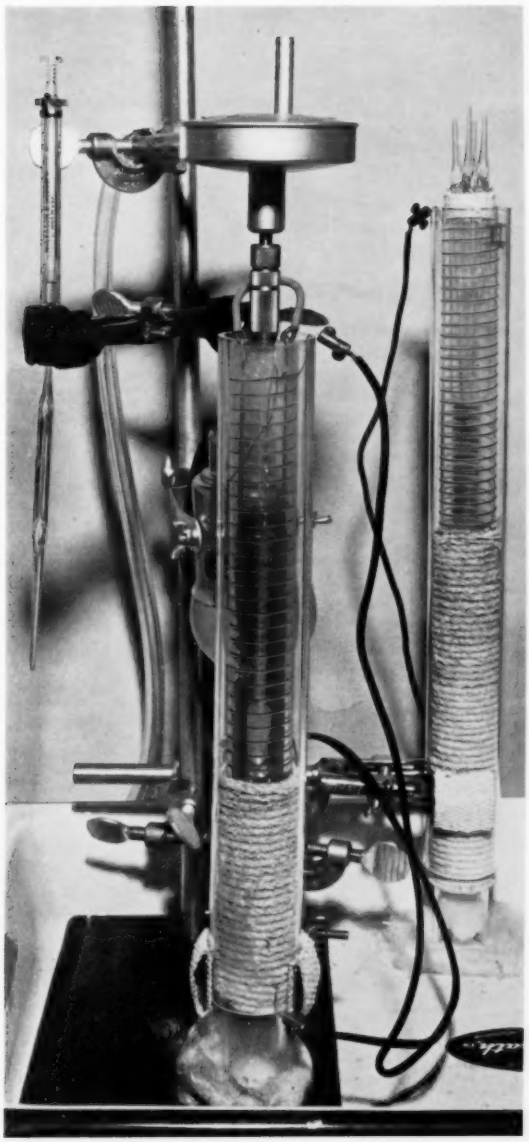

FIG. A.—View of the extraction apparatus.

and CLARK[2] and by PROTSENKO[3]. The composition of the eutectic mixture is 43 mole per cent lithium nitrate and 57 mole per cent potassium nitrate with a melting point of 120°C.

The initial extractant chosen for this study was *n*-butyl phosphate (TBP) because of its high boiling point, negligible solubility in the lithium nitrate-potassium nitrate salt phase and its relatively good thermal stability. The extraction behaviour of TBP in aqueous systems has been studied very thoroughly[4] and it was hoped that fruitful comparisons could be made between the aqueous and fused salt systems.

An inert organic diluent had to be chosen in order to study the solvent dependency of the metal ions. The following properties were required of the diluent: thermal stability, high boiling point, inertness to chemical attack by molten nitrates, complete miscibility with TBP, liquid at room temperature, and possessing an appropriate density to promote mixing and separation of phases. The polyphenyl aromatic hydrocarbons met these requirements. Although the pure compounds are solids at room temperature, appropriate mixtures are known to form low melting eutectics. The composition chosen (in weight per cent) was the eutectic mixture[5] 25 per cent biphenyl, 55 per cent ortho-terphenyl, and 20 per cent meta-terphenyl. The properties of this mixture are summarized in Table 1.

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TABLE 1.—PROPERTIES OF THE EUTECTIC MIXTURE OF POLYPHENYLS

| | |
|---|---|
| Density at 150°C | 0·962 g/cm³ |
| Viscosity at 150°C | 1·10 cP |
| Melting point | 10·6°C |
| Boiling point | 298°C |
| Vapour pressure at 150°C | 9·0 mm of Hg |
| Solubility in TBP | Miscible in all proportions |

Various ions such as $SO_4^{2-}$, $PO_4^{3-}$, $SCN^-$, $F^-$ and $Cl^-$ held promise as complexing agents in the fused salt phase. Chloride ion was chosen first since some information concerning its complexing powers in nitrate melts is available[1]. Most of the metal ions were studied both in pure $LiNO_3$–$KNO_3$ eutectic as well as in a $LiNO_3$–$KNO_3$ eutectic containing varying concentrations of chloride ion.

## EXPERIMENTAL PROCEDURE

1. *Design of the apparatus.* A simple apparatus was designed for contacting the salt and the organic solvent (Fig. A). An 18 in. long, 1 in. diameter vycor heater mantle was spirally grooved on the outside along its entire length. The grooves were 1 mm in width and 1 mm in depth. Nichrome wire (0·5 mm diameter) was wound in the grooves and connected to a Variac. In order to minimize the loss of heat, the Vycor mantle was enclosed in a Pyrex sleeve. Contact between the two immiscible phases was established in a 12 ml Pyrex centrifuge tube. A brass liner suspended inside the mantle and shaped to hold the centrifuge tube helped maintain a constant temperature along the entire length of the tube. Two narrow slits directly opposite each other in the brass liner made it possible to observe the extraction process visually. In each experiment, the centrifuge tube was placed in the same position inside the mantle by suspending it from a brass linkage resting on the metallic liner (Fig. B). The two

[2] W. D. HARKINS and G. L. CLARK, *J. Amer. Chem. Soc.* **37**, 1816 (1915).
[3] P. I. PROTSENKO, *J. Gen. Chem. (USSR)* **22**, 1357 (1952).
[4] F. R. BRUCE, J. M. FLETCHER and H. H. HYMAN, *Progress in Nuclear Energy*, Series III, Vol. 2, Appendix III. Pergamon Press, Oxford (1958).
[5] Radiation resistant fluids, *Monsanto Bull.*

liquid phases were stirred with a Pyrex rod driven by an air stirrer. The entire apparatus was placed in a hood for work with radioactive substances.

2. *Temperature stability of the heating mantle.* The operating temperature in the heating mantle was maintained at 150 ± 1°C with a Variac without additional temperature controls. Approximately 60 min were required for the salt mixture to melt and reach a temperature of 150°C. Measurements taken at different heights in the liquid showed a uniform temperature.

3. *Preparation of the lithium nitrate–potassium nitrate eutectic.* The mixture used in the experiments, composed of 43 mole per cent lithium nitrate and 57 mole per cent potassium nitrate (Baker

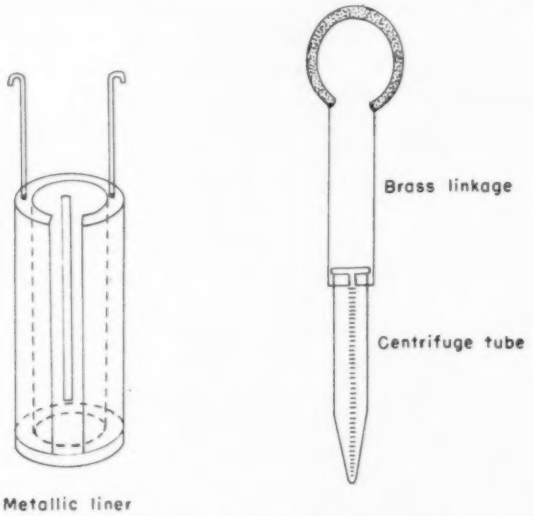


FIG. B.—Sketch of the metallic liner and the brass linkage holding a centrifuge tube.

analysed reagent), was melted at a temperature of 350°C and maintained at 150°C for a 24 hr period while bubbling dry nitrogen gas through the molten salt to insure removal of water. The mixture was maintained at 150°C and utilized as such or cooled, cast into pellets and stored in a dry atmosphere. The density of this mixture was determined at 150°C and found to be 1·948 g/cm³.[6]

4. *Preparation of lithium nitrate–potassium nitrate melt containing lithium chloride–potassium chloride.* Lithium nitrate–potassium nitrate mixtures containing varying concentrations of chloride ion were prepared by adding known weights of lithium chloride–potassium chloride mixtures, in which the lithium–potassium ratios were the same as in the nitrate mixture. The samples so prepared were analysed for their chloride content. Two concentrations were used:

(1) 0·43 molal in chloride ions, density at 150°C = 1·956 g/cm³.
(2) 0·24 molal in chloride ions, density at 150°C = 1·953 g/cm³.

5. *Preparation of the organic phase.* Tributyl phosphate, was purified in the manner described by PEPPARD *et al.*[7] The temperature stability of TBP was verified in the following manner: 5 ml of TBP was placed inside a tube in the heating mantle and maintained for 3 hr at a temperature of 175°C. This sample of TBP was then utilized for a determination of the distribution coefficient of uranium nitrate at 25°C in an aqueous solution of nitric acid. The value of the distribution coefficient found in this experiment agreed well with that obtained under the same experimental conditions using TBP which had not been heated. Degradation of TBP by temperature would probably have increased the distribution coefficient of uranium due to the formation of dibutyl phosphate and mono-butyl phosphate. However, TBP in contact with molten $LiNO_3$–$KNO_3$ eutectic is slowly attacked and becomes viscous after several hours at 150°C. In all the experiments, therefore, the time of contact of the TBP with the molten salt phase was held to a few minutes.

[6] D. M. GRUEN and R. L. MCBETH, *J. Phys. Chem.* **63**, 393 (1959)
[7] D. F. PEPPARD, W. J. DRISCOLL, R. J. SIRONEN and S. MCCARTY, *J. Inorg. Nucl. Chem.* **4**, 326 (1957).

The inert organic diluent eutectic of biphenyl, *o*-terphenyl and *m*-terphenyl was prepared from commercial products without further purification. The mixture was melted at a temperature of 100°C, cooled to room temperature and then used.

To show that the diluent itself does not extract metal ions, a distribution coefficient of U(VI) between the $LiNO_3$–$KNO_3$ molten phase and the pure diluent as the organic phase was determined. Less than 0·1 per cent of the uranium was found in the organic phase at equilibrium.

6. *Determination of the distribution coefficients.* All the distribution coefficients, with the exception of lithium and potassium, were determined in the following manner: a known weight of metal nitrate was introduced into the centrifuge tube. A measured quantity of the appropriate radioactive tracer was added as the soluble nitrate and the solution evaporated to dryness in a vacuum dessicator. A known weight of the $LiNO_3$–$KNO_3$ eutectic mixture equivalent to approximately 1 ml of melt, was added to the tube suspended in the heating mantle. When a temperature of 150°C was reached, the mixture was stirred in order to obtain a homogeneous solution. In certain cases, dissolution of the metal nitrate was slow and therefore the stirring time depended on the particular metal ion present. One ml of preheated TBP, which had previously been pre-equilibrated with respect to the barren molten salt phase, was added, and the two phases were stirred for 2 or 3 min with an air stirrer. When the two phases had completely separated, the TBP phase was withdrawn from the tube and cooled at room temperature. Samples were then taken to determine the concentration of the metal. A known quantity ($\approx$ 0·1 to 0·2 g) of the fused salt phase was removed with the aid of a preheated micropipette, and the aliquot introduced into a weighed graduated 1 ml tube. The tube containing the solidified salt was weighed at room temperature and the salt dissolved in 1 ml of dilute nitric acid to determine the metal ion concentration.

7. *Determination of metal ion concentration.* The metal ion concentration in both phases at equilibrium was determined except for lithium and potassium, by measuring the activity of the radioactive isotope present. Samples of 1–25 $\mu$l (depending on the quantity of activity present) were withdrawn and deposited on 3 mil platinum plates. The aliquot was evaporated slowly to dryness and the plate heated to about 600°C by induction heating. These plates were then counted in an alpha or beta counter depending on the tracer present.

8. *Determination of the lithium and potassium distribution coefficients.* The distribution coefficients of lithium and potassium were determined in the following manner: the melted eutectic mixture at 150°C was contacted with an equal volume of TBP. After complete separation, the TBP phase was withdrawn and cooled to room temperature. A known volume of the TBP was stripped three times with equal volumes of a very dilute nitric acid solution (0·07 M) and the combined aqueous phases were analysed by flame photometry for their lithium and potassium content. The distribution coefficients were calculated by subtracting the concentrations of lithium and potassium found in the organic phase from the original concentrations of lithium and potassium in the fused salt phase. Quantitative recovery during the strip operation was confirmed in experiments using radioactive tracers.

9. *Preparation and purification of radioactive tracers.* The following radioactive tracers were used in this research: $^{60}$Co, $^{147}$Nd, $^{154}$Eu, $^{233}$U, $^{237}$Np, $^{241}$Am and $^{244}$Cm. $^{60}$Co, $^{147}$Nd, and $^{154}$Eu were prepared by neutron activation of stable isotopes and purified by solvent extraction and ion exchange techniques. $^{233}$U was obtained from irradiated thorium and purified by solvent extraction.* $^{237}$Np was prepared from plutonium irradiated at Hanford and purified by solvent extraction. $^{241}$Am was separated by extracting the americium resulting from $\beta$-decay of $^{241}$Pu. $^{244}$Cm was prepared by irradiating $^{239}$Pu in the Materials Testing Reactor and purified by ion exchange methods.

## RESULTS AND DISCUSSION

### 1. *Determination and general expressions for the over-all distribution coefficients of metal nitrates distributed between a lithium–potassium nitrate phase and an organic phase containing tributyl phosphate*

(a) *Results.* Distribution coefficients of many different elements have been

* $^{233}$U was kindly furnished to us by F. T. HAGEMANN.

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determined in aqueous systems between a nitrate phase and a diluted TBP phase.[7–22] It appears that the distribution coefficients increase with increasing net charges of the ions. Some distribution coefficients are as low as $10^{-6}$, but can be enhanced by increasing the nitrate ion concentration through addition of salting out agents to the aqueous phase.

As mentioned previously, preliminary results[1] showed that quantitative extraction of nitrates into pure TBP could be obtained from a molten nitrate eutectic.

In this investigation, a series of distribution coefficients for ions in different oxidation states, were measured using molten $LiNO_3$–$KNO_3$ eutectic (150°C) and TBP diluted with a mixture of polyphenyls. Results are summarized in Table 2.

The value of $[TBP]_o^e$, or the concentration of free TBP at equilibrium in the organic phase, was calculated from the initially present TBP concentration $[TBP]_o^i$ by the following expression:

$$[TBP]_o^e = [TBP]_o^i - [TBP]_o^c$$

where $[TBP]_o^c$, the concentration of TBP complexed by the metal was obtained by assuming that the number of TBP molecules associated with each molecule of complexed electrolyte in the organic phase, was identical to that found in aqueous systems (cf. Table 5). An exception was Co(II), where better results could be obtained by assuming that only two molecules of TBP were complexed by each molecule of cobalt nitrate extracted. The calculations of $[TBP]_o^e$ were corrected for the Li(I) concentrations in the organic phase which were determined in separate experiments (see Table 2). It was assumed that the concentration of Li(I) in the organic phase is unperturbed by the extraction of other metal ions.

The distribution coefficients reported in Table 2, have much higher values than the values reported for comparable aqueous nitric acid systems. For example, the following results were obtained for the distribution coefficients of Eu(III) extracted from a 15·6 M $HNO_3$ solution into TBP, diluted with kerosene:[15]

| TBP conc. (%) | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Distrib. coeff. Eu(III) | 0·00029 | 0·0024 | 0·0076 | 0·0174 | 0·032 |

Comparing these values with those of Table 2 it can be seen that the fused salt

[8] D. F. PEPPARD, J. FARIS, P. GRAY and G. MASON, *J. Phys. Chem.* **57**, 294 (1953).
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[10] D. F. PEPPARD, G. MASON and J. MAIER, *J. Inorg. Nucl. Chem.* **3**, 215 (1956).
[11] K. ALCOCK, S. GRIMLEY, T. HEALY, J. KENNEDY and H. MCKAY, *Trans. Faraday Soc.* **52**, 39 (1956).
[12] E. HESFORD and H. MCKAY, *Trans. Faraday Soc.* **54**, 573 (1958).
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[15] D. SCARGILL, K. ALCOCK, J. FLETCHER, E. HESFORD and H. MCKAY, *J. Inorg. Nucl. Chem.* **4**, 304 (1957).
[16] G. BEST, H. MCKAY and P. WOODGATE, *J. Inorg. Nucl. Chem.* **4**, 315 (1957).
[17] E. HESFORD, H. MCKAY and D. SCARGILL, *J. Inorg. Nucl. Chem.* **4**, 321 (1957).
[18] K. ALCOCK, G. BEST, E. HESFORD and H. MCKAY, *J. Inorg. Nucl. Chem.* **6**, 328 (1958).
[19] T. SATO, *J. Inorg. Nucl. Chem.* **6**, 334 (1958).
[20] J. C. WARF, *J. Amer. Chem. Soc.* **71**, 3257 (1949).
[21] T. V. HEALEY and H. A. C. MCKAY, *Rec. Trav. Chim.* **75**, 730 (1956).
[22] T. V. HEALEY and P. E. BROWN, AERE/C/R 1970 (1956).

TABLE 2.—DISTRIBUTION COEFFICIENTS OF DIFFERENT METAL NITRATES BETWEEN A $LiNO_3$–$KNO_3$ PHASE AND A DILUTED TBP PHASE, AT 150°C

| Metal ion | Initial metal ion conc. in molten salt (M) | $[TBP]_0^i$ (M) | $[TBP]_0^e$ (M) | $K'_d$ |
|---|---|---|---|---|
| Li(I) | 9·495 | 0·037 | 0·035 | $8·0 \pm 0·8 \times 10^{-5}$ |
| | | 0·074 | 0·067 | $3·3 \pm 0·3 \times 10^{-4}$ |
| | | 0·092 | 0·084 | $4·5 \pm 0·4 \times 10^{-4}$ |
| | | 0·148 | 0·126 | $1·1 \pm 0·1 \times 10^{-3}$ |
| | | 0·184 | 0·152 | $1·6 \pm 0·2 \times 10^{-3}$ |
| | | 0·369 | 0·280 | $4·8 \pm 0·5 \times 10^{-3}$ |
| | | 0·922 | 0·570 | $1·9 \pm 0·2 \times 10^{-2}$ |
| | | 3·69 (100% TBP) | 0·29 | 0·22 ± 0·02 |
| K(I) | 12·7 | 0·037 | 0·035 | $10^{-6}$ |
| | | 0·074 | 0·067 | $10^{-6}$ |
| | | 0·092 | 0·084 | $10^{-6}$ |
| | | 0·148 | 0·126 | $10^{-5}$ |
| | | 0·184 | 0·152 | $10^{-5}$ |
| | | 0·369 | 0·280 | $10^{-5}$ |
| | | 0·922 | 0·570 | $10^{-4}$ |
| Co(II) | 0·053 | 0·037 | 0·032 | $2·0 \pm 0·1 \times 10^{-2}$ |
| | 0·092 | 0·074 | 0·057 | $6·7 \pm 0·4 \times 10^{-2}$ |
| | 0·045 | 0·148 | 0·102 | 0·36 ± 0·02 |
| | 0·069 | 0·184 | 0·115 | 0·38 ± 0·03 |
| | 0·080 | 0·369 | 0·190 | 1·15 ± 0·08 |
| | 0·057 | 0·369 | 0·214 | 1·5 ± 0·1 |
| | 0·058 | 0·922 | 0·470 | 7·8 ± 0·5 |
| Nd(III) | $5·94 \times 10^{-3}$ | 0·074 | 0·060 | 0·35 ± 0·02 |
| | | 0·092 | 0·077 | 0·60 ± 0·04 |
| | | 0·148 | 0·117 | 1·38 ± 0·09 |
| | | 0·148† | 0·113 | 2·1 ± 0·1 |
| | | 0·184 | 0·151 | 4·0 ± 0·3 |
| Eu(III) | $6·7 \times 10^{-3}$ | 0·037 | 0·032 | 0·23 ± 0·02 |
| | | 0·074 | 0·056 | 0·69 ± 0·05 |
| | | 0·092 | 0·070 | 1·8 ± 0·1 |
| | | 0·148 | 0·110 | 5·9 ± 0·4 |
| | | 0·184 | 0·133 | 13·3 ± 0·9 |
| | | 0·184† | 0·133 | 16 ± 1 |
| | | 0·184† | 0·133 | 13·3 ± 0·9 |
| Am(III) | $^{241}Am$ tracer | 0·092 | 0·075 | 0·43 ± 0·03 |
| | | 0·148 | 0·113 | 1·4 ± 0·1 |
| | Eu carrier | 0·184 | 0·140 | 3·8 ± 0·3 |
| | $4·74 \times 10^{-3}$ | 0·369 | 0·264 | 24 ± 2 |

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TABLE 2 (Continued).

| Metal ion | Initial metal ion conc. in molten salt (M) | $[TBP]_o^i$ (M) | $[TBP]_o^e$ (M) | $K'_d$ |
|---|---|---|---|---|
| Cm(III) | $^{244}$Cm tracer<br>Nd carrier<br>$6{\cdot}0 \times 10^{-3}$ | 0·037<br>0·074<br>0·092 | 0·034<br>0·063<br>0·077 | 0·13 ± 0·09<br>0·84 ± 0·06<br>1·4 ± 0·1 |
| Np(VI) | 0·002 | 0·074 | 0·064 | > 50 |
| U(VI) | 0·01 | 0·037 | 0·027 | 8·3 ± 0·6 |
| | 0·054 | 0·074 | 0·006 | 1·4 ± 0·1 |
| | 0·033 | 0·074 | 0·010 | 7·5 ± 0·5 |
| | 0·010 | 0·074 | 0·050 | 17 ± 1 |
| | 0·050 | 0·092 | 0·010 | 3·0 ± 0·2 |
| | 0·010 | 0·092 | 0·064 | 25 ± 2 |
| | 0·053 | 0·148 | 0·028 | 11·3 ± 0·8 |
| | 0·053 | 0·148† | 0·028 | 22 ± 1 |
| | 0·054 | 0·148† | 0·028 | 9·0 ± 0·6 |

$[TBP]_o^i$ = initial TBP concentration, mole/l.
$[TBP]_o^e$ = free TBP concentration at equilibrium.
$K'_d$ = experimentally determined distribution coefficient (o/s).
† = repeat experiments.

values are about $10^2$ times greater. It should be noted that the nitrate concentration of the $LiNO_3$–$KNO_3$ eutectic is 22·4 M.

For Li(I) and K(I) the distribution coefficients given in Table 2 were obtained contacting the $LiNO_3$–$KNO_3$ eutectic phase, with the organic phase. The high value of 0·024 M obtained in this experiment for the solubility of K(I) in pure TBP should not be compared with the value 0·0063 M obtained by saturating pure TBP at 150°C with $KNO_3$ alone. The presence of $LiNO_3$ in the molten salt phase apparently increases concentration of K(I) in the organic phase. A similar "salting out" effect has been noticed earlier in aqueous systems.[22] The solubility of Li(I) on the other hand is little affected by the presence of $KNO_3$. The value given in Table 2 is 1·7 M in pure TBP at 150°C, which is to be compared with the values 1·32 M at 25°C and 1·56 M at 50°C found by HEALY and BROWN[22] in the absence of $KNO_3$.

All the distribution coefficients listed in Table 2 were determined using concentrations of metal ions in the range $10^{-3}$ M or with tracer concentrations supported by a suitable carrier. Carriers were found to be necessary to maintain tracer quantities of any of the elements investigated in the molten salt solutions. A reaction between the molten $LiNO_3$–$KNO_3$ phase and the Pyrex container was postulated to account for the lack of material balances when tracer quantities of metal ions were used without carrier. Different container materials such as quartz, Teflon and stainless steel were tried, without significantly changing the results obtained with Pyrex. The material balance was, however, improved with quartz. The best results were obtained when a Pyrex tube, which had been contacted two or three times with the molten salt phase, was employed with the radioactive tracer. This effect is being further investigated.

Metal ions representative of the (IV) oxidation state [Th(IV)] and of the (V) oxidation state [Np(V)] are still under study.

(b) *Discussion.* Information obtained from aqueous nitrate extractions with TBP have led to the postulate that the complexes extracted into the organic phase are of the type $M(NO_3)_p(TBP)_q$. The equilibrium reaction is generally formulated as:[21]

$$M_a^{p+} + p\ NO_{3a}^- + q\ TBP_o \rightleftharpoons \{M(NO_3)_p(TBP)_q\}_o \tag{1}$$

where $a$ = aqueous phase
O = organic phase

Neglecting activity coefficients, the complex constant $k_c$ is given by:

$$k_c = \frac{[M(NO_3)_p(TBP)_q]_o}{[M^{p+}]_a[NO_3^-]_a^p[TBP]_o^q} \tag{2}$$

where the brackets [ ] stand for concentration. Since the distribution coefficients, $k_d$, of a metal is defined by the ratio of the concentration of the metal in the organic phase to the concentration of the metal in the aqueous phase at equilibrium, it follows that:

$$k_c = \frac{k_d}{[NO_3^-]_a^p[TBP]_o^q} \tag{3}$$

or

$$k_d = k_c[NO_3^-]_a^p[TBP]_o^q \tag{4}$$

Similar equilibrium equations should be applicable to a system where the metal is distributed between a molten salt phase and TBP.

Reaction (1) assumes that all the metal in the organic phase is in the form of the complex $[M(NO_3)_p(TBP)_q]_o$. Furthermore, reaction (1) does not take into account possible undissociated species of the form $M(NO_3)_p$ in the salt phase or species which are not complexed by TBP in the organic phase. The following set of equilibrium equations take these possibilities into account:

$$M_s^{p+} + pNO_{3s}^- \rightleftharpoons \{M(NO_3)_p\}_s \tag{5}$$

$$\{M(NO_3)_p\}_s \rightleftharpoons \{M(NO_3)_p\}_o \tag{6}$$

$$\{M(NO_3)_p\}_o + qTBP_o \rightleftharpoons \{M(NO_3)_p(TBP)_q\}_o \tag{7}$$

where the subscripts "s" and "o" refer to salt phase and organic phase respectively.

To each of these equations correspond an equilibrium constant, $K_e$, $K_d$, $K_c$ which, neglecting again activity coefficients, may be defined as:

$$K_e = \frac{[M(NO_3)_p]_s}{[M^{p+}]_s[NO_3^-]_s^p} \tag{8}$$

$$K_d = \frac{[M(NO_3)_p]_o}{[M(NO_3)_p]_s} \tag{9}$$

$$K_c = \frac{[M(NO_3)_p(TBP)_q]_o}{[M(NO_3)_p]_o[TBP]_o^q} \tag{10}$$

The experimentally measured distribution coefficient $K_d'$ is equal to the ratio of the total concentration of the metal in the organic phase over the total concentration in

the salt phase. It may be expressed, using the previously defined equilibrium constants, by the following equation:

$$K_d' = K_d \frac{\{1 + K_e[\text{TBP}]_o{}^q\}}{\left\{1 + \frac{1}{K_e[\text{NO}_3^-]_s{}^p}\right\}} \tag{11}$$

In most experimental cases, where pre-equilibriated organic phases were used, the nitrate concentration $[NO_3^-]_s$ may be assumed constant so that (11) becomes:

$$K_d' = \frac{K_d}{K_e'} \{1 + K_e[\text{TBP}]_o{}^q\} \tag{12}$$

where

$$K_e' = 1 + \frac{1}{K_e[\text{NO}_3^-]_s{}^p} \tag{13}$$

Because little is known about the value of $K_e$, it is not possible to predict if $K_e'$ differs considerably from unity.

Under certain circumstances equation (12) may be further simplified. In fact for all systems where $K_e[\text{TBP}]_o{}^q \gg 1$, the following relation, similar to (4), holds:

$$\log K_d' = \log \frac{K_d K_e}{K_e'} + q \log [\text{TBP}]_o \tag{14}$$

For systems obeying equation (14) a plot of $\log K_d'$ vs. $\log [\text{TBP}]_o$ should give a straight line of slope $q$, where $q$ is the number of TBP molecules associated with the metal complex. For all other systems, equation (12) should be applied as will be shown later.

2. *Determination of distribution coefficients of metal nitrates between lithium nitrate–potassium nitrate eutectic containing chloride ions and an organic phase containing tributyl phosphate*

Molten lithium nitrate–potassium nitrate eutectic containing different concentration of chloride ions has been used as a solvent system in the study of chloro-complexes of Co(II) and Ni(II) by spectrophotometric techniques.[1] Stepwise complex formation occurs from "uncomplexed" Co(II) in melts containing no added chloride ion to "fully complexed" $CoCl_4^{2-}$ in the presence of 1 M added chloride ion. In view of these observations it was of interest to study the effect of added chloride ions on the distribution coefficients of the metal nitrates studied in the pure nitrate melt. Table 3 summarizes the results of the studies.

No influence on the distribution coefficients of Li(I) and K(I) was found by adding chloride ions up to a concentration of 0·43 molal. Hence, the values of $[\text{TBP}]_o{}^e$ in Table 3 were obtained using the results reported in Table 2 for the Li(I) and K(I) content in the organic phase. For all other metal ions studied, the distribution coefficients decrease on addition of chloride ions to the nitrate melts. COLLOPY[24] has observed a similar effect in the extraction of $UO_2^{2+}$ from aqueous nitrate solutions to which $SO_4^{2-}$ has been added.

[23] D. M. GRUEN and E. BERTAUT, Private communications (1960).
[24] T. J. COLLOPY and D. A. STOCK, NLCO 801 (1960).

TABLE 3.—DISTRIBUTION COEFFICIENTS OF DIFFERENT METAL NITRATES BETWEEN A $LiNO_3$–$KNO_3$ PHASE CONTAINING CHLORIDE IONS AND A DILUTED TBP PHASE, AT 150°C

| Metal ion | Initial metal ion conc. in molten salt (M) | $[TBP]_o^i$ (M) | $[TBP]_o^e$ (M) | $K_d'$ |
|---|---|---|---|---|
| **Chloride ions: 0·43 molal** | | | | |
| Co(II) | 0·04 | 0·092 | 0·09 | 0·016 ± 0·001 |
| | 0·097 | 0·148 | 0·120 | 0·038 ± 0·003 |
| | 0·052 | 0·184 | 0·146 | 0·068 ± 0·005 |
| | 0·068 | 0·369 | 0·256 | 0·19 ± 0·01 |
| | 0·077 | 0·922 | 0·503 | 0·73 ± 0·05 |
| Nd(III) | $5·94 \times 10^{-3}$ | 0·074 | 0·064 | 0·25 ± 0·02 |
| | | 0·092 | 0·086 | 0·43 ± 0·03 |
| | | 0·148 | 0·113 | 1·32 ± 0·09 |
| Eu(III) | $6·26 \times 10^{-3}$ | 0·092 | 0·073 | 1·41 ± 0·09 |
| | | 0·148 | 0·110 | 5·3 ± 0·4 |
| | | 0·184 | 0·137 | 13·1 ± 0·9 |
| Am(III) | $^{241}$Am tracer Eu carrier $6·26 \pm 10^{-3}$ | 0·092 | 0·073 | 0·130 ± 0·009 |
| | | 0·148 | 0·110 | 0·57 ± 0·04 |
| | | 0·184 | 0·137 | 1·32 ± 0·09 |
| | | 0·369 | 0·265 | 10·1 ± 0·7 |
| Cm(III) | $^{244}$Cm tracer Nd carrier $6·0 \times 10^{-3}$ | 0·148 | 0·116 | 1·9 ± 0·1 |
| U(VI) | 0·038 | 0·184 | 0·079 | 24 ± 2 |
| **Chloride ions: 0·24 molal** | | | | |
| Co(II) | 0·045 | 0·074 | 0·066 | 0·021 ± 0·001 |
| | | 0·148 | 0·120 | 0·081 ± 0·005 |
| | | 0·184 | 0·142 | 0·128 ± 0·009 |
| Am(III) | $^{241}$Am tracer Eu carrier $4·74 \times 10^{-3}$ | 0·092 | 0·075 | 0·21 ± 0·01 |
| | | 0·148 | 0·114 | 1·09 ± 0·08 |
| Cm(III) | $^{244}$Cm tracer Nd carrier $6·0 \times 10^{-3}$ | 0·092 | 0·077 | 0·95 ± 0·06 |
| | | 0·148 | 0·115 | 3·3 ± 0·4 |

$[TBP]_o^i$ = initial TBP concentration, moles/l.
$[TBP]_o^e$ = free TBP concentration at equilibrium.
$K_d'$ = experimentally determined distribution coefficient (o/s).

### 3. *Determination of distribution coefficients between a* $LiNO_3$–$KNO_3$ *phase containing* $NH_4NO_3$ *and an organic phase containing tributyl phosphate*

The difficulty in obtaining material balances when working with tracer concentration of elements in the molten salt phase, led to the hypothesis of a possible instability



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of the metal nitrates. Recently, it has been found [23] that it is possible to convert metal oxides into metal nitrates in molten $LiNO_3$–$KNO_3$ eutectic by using a stoicheiometric amount of $NH_4NO_3$. For example in the case of uranium the following reaction occurs:

$$UO_3 + 2NH_4NO_3 \rightarrow UO_2(NO_3)_2 + 2NH_3\uparrow + H_2O.$$

In this investigation $NH_4NO_3$ was added to tracer concentrations of Am(III), Cm(III) and U(VI) dissolved in a $LiNO_3$–$KNO_3$ eutectic salt to see if the metal ion could be maintained in solution quantitatively.

TABLE 4.—DISTRIBUTION COEFFICIENTS OF DIFFERENT METAL NITRATES BETWEEN A $LiNO_3$–$KNO_3$ PHASE CONTAINING $NH_4NO_3$ (1·4 PER CENT BY WEIGHT) AND A DILUTED TBP PHASE AT 150°C

| Metal ion | Initial metal ion conc. in molten salt (M) | $[TBP]_o^i$ (M) | $[TBP]_o^e$ (M) | $K_d'$ |
|---|---|---|---|---|
| Am(III) | $^{241}$Am tracer | 0·092 | 0·084 | 10·3 ± 0·07 |
| Cm(III) | $^{244}$Cm tracer | 0·074 | 0·067 | 4·7 ± 0·3 |
| U(VI) | $^{233}$U tracer | 0·037 | 0·036 | > 30 |

$[TBP]_o^i$ = initial TBP concentration, moles/l.
$[TBP]_o^e$ = free TBP concentration at equilibrium.
$K_d'$ = experimentally determined distribution coefficient (o/s).

The results showed that the radioactive tracer dissolved quantitatively in the molten salt phase. Distribution coefficients were determined by contacting the resulting salt solutions with different concentrations of TBP. The data are summarized in Table 4. Marked increases in the distribution coefficients were observed compared with those obtained in pure $LiNO_3$–$KNO_3$ eutectic. These observations cannot as yet be explained in detail.

An experiment in which milligram amounts of Np were dissolved in a $LiNO_3$–$KNO_3$ eutectic showed all of the Np to be in the (V) oxidation state by spectrophotometric analysis*. A distribution coefficient determined on an aliquot of this solution with 1% TBP gave a value of $K_d'$ equal to 0·0045. A small amount of $NH_4NO_3$ was then added to the remainder of the melt and the spectrum remeasured at regular intervals for 24 hr. A very marked decrease of the characteristic peak of the (V) oxidation state (983 m$\mu$) occurred as a function of time. After 24 hr, the peak height was only 10 per cent of its original value. Owing to the small molar absorption coefficient of Np(VI) the quantity of Np in the (VI) state could not be determined directly. However, a distribution coefficient determined on an aliquot of the melt with 1% TBP gave a value of 3·6 indicating the formation of Np(VI). A melt containing Np, to which no $NH_4NO_3$ had been added gave a distribution coefficient of 0·0045 with 1% TBP even after 8 days, showing that under these conditions Np(V) is the stable oxidation state in the molten salt phase. Later investigations by COHEN confirmed the assignment of the neptunium oxidation states.[25]

* All the spectrophotometric analyses were kindly performed by W. T. CARNALL and D. COHEN.

[25] D. COHEN, Private communications (1960).

4. *Determination of the nature of the complexes formed in the organic phase*

Looking at equations (12) and (14) it is seen that the solvation number $q$ can be found by plotting, in the first case, a curve of $\log\left(K_d' - \frac{K_d}{K_e'}\right)$ vs. $\log [TBP]_o^q$ and, in the second case, $\log K_d'$ vs. $\log [TBP]_o^q$. This solvation number indicates the number of TBP molecules per molecule of complexed electrolyte in the organic phase. The value of $q$ has been determined for numerous nitrates extracted from an aqueous phase into TBP. Table 5 summarizes these results.

It has been demonstrated in aqueous systems that the relation (14) was only valuable for concentrations of less than 10% TBP by volume. Above this concentration, important deviations appeared because of non-ideality of the organic phase.

This fact presented problems in aqueous systems because in numerous cases the

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TABLE 5.—NUMBER OF TBP MOLECULES PER MOLECULE OF COMPLEXED ELECTROLYTE IN THE ORGANIC PHASE OR $q$[18]

| Nitrates | $q$ |
|---|---|
| $LiNO_3$ | 2 |
| $NaNO_3$ | 3 |
| $Ca(NO_3)_2$ | 3 |
| $Co(NO_3)_2$ | 3 |
| $(Y, Ce, Am)(NO_3)_3$ | 3 |
| $(Zr, Ce, Th, Np, Pu)(NO_3)_4$ | 2 |
| $(U, Np, Pu)O_2(NO_3)_2$ | 2 |

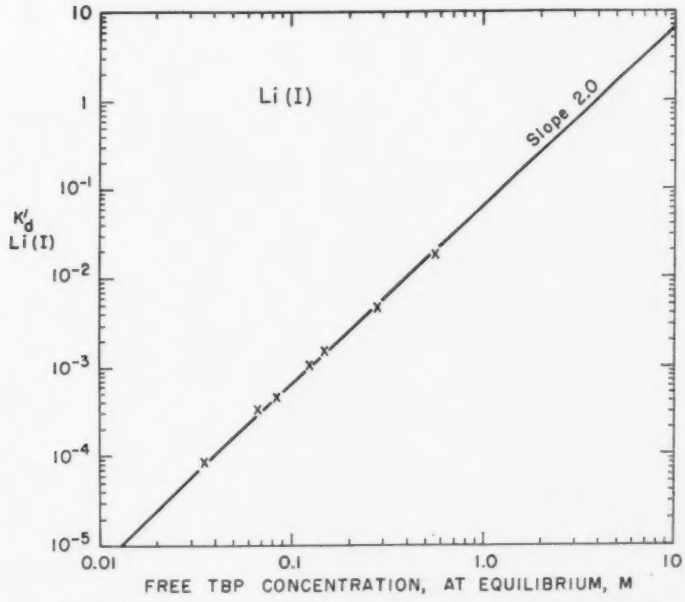


FIG. 1.—The distribution coefficients ($K_d'$) of Li(I) in a pure nitrate melt or in a nitrate–chloride melt, as a function of free TBP concentration at equilibrium

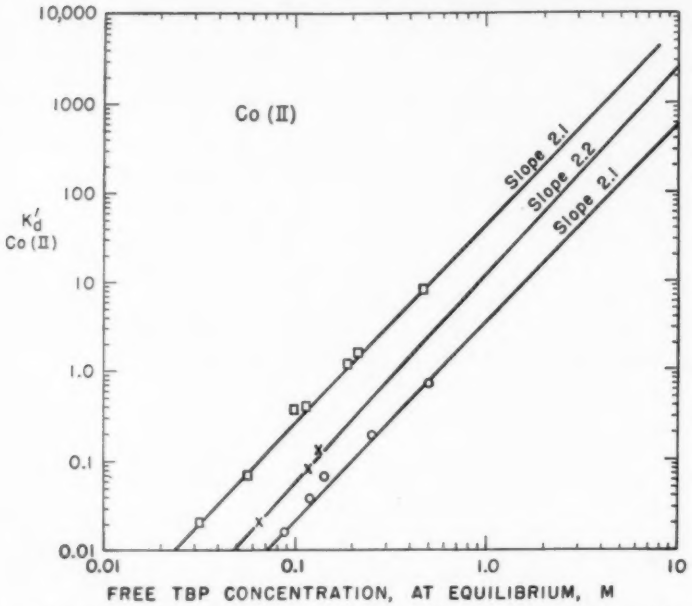


FIG. 2.—The distribution coefficients ($K_d'$) of Co(II) in a nitrate melt and in a nitrate–chloride melt, as a function of free TBP concentration at equilibrium.
□ pure nitrate melt.
× 0·24 molal in chloride ions.
○ 0·43 molal in chloride ions.

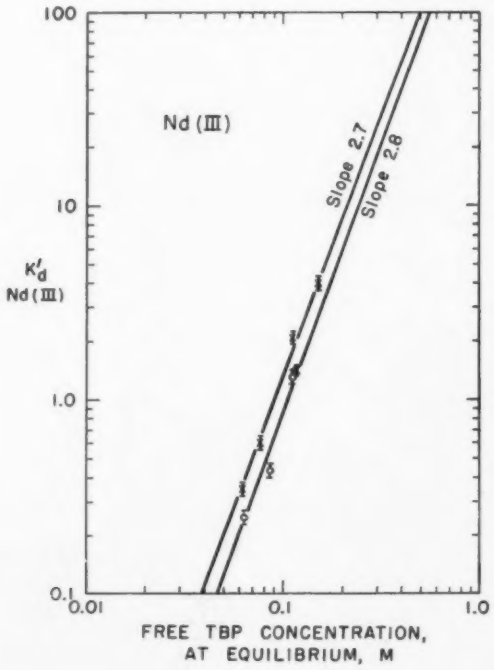


FIG. 3.—The distribution coefficients ($K_d'$ of Nd(III) as a function of free TBP concentration at equilibrium.
× pure nitrate melt.
○ nitrate melt containing 0·43 molal chloride ions.

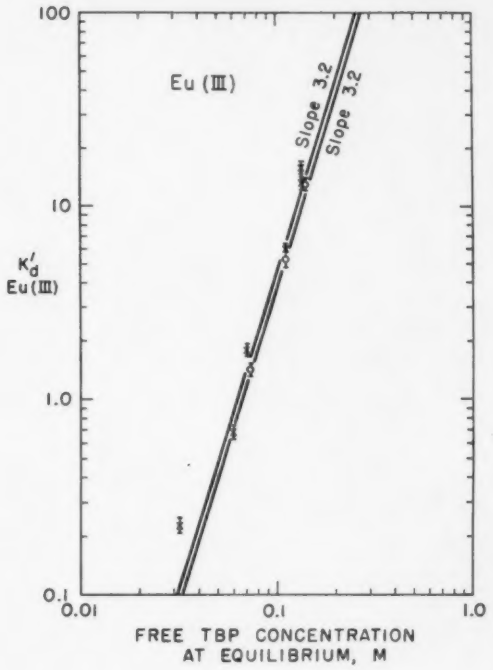


FIG. 4.—The distribution coefficients ($K_d'$) of Eu(III) as a function of free TBP concentrations at equilibrium.
× pure nitrate melt.
○ nitrate melt containing 0·43 molal chloride ions.

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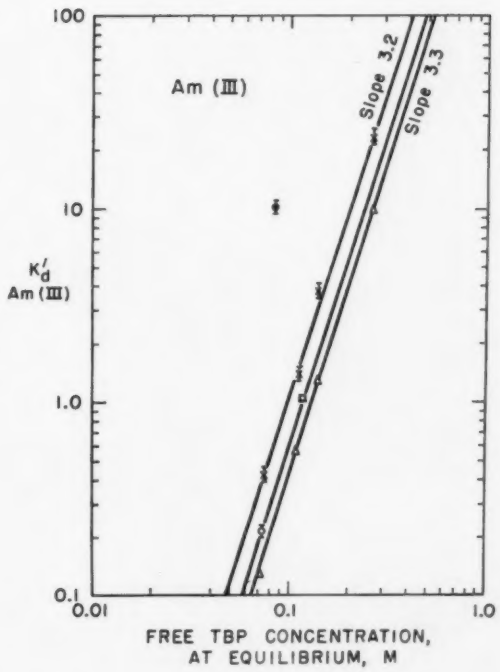


FIG. 5.—The distribution coefficients ($K_d'$) of Am(III) as a function of free TBP concentration at equilibrium.
× pure nitrate melt.
○ nitrate melt containing 0·24 molal chloride ions.
Δ nitrate melt containing 0·43 molal chloride ions.
Φ nitrate melt containing $NH_4NO_3$.

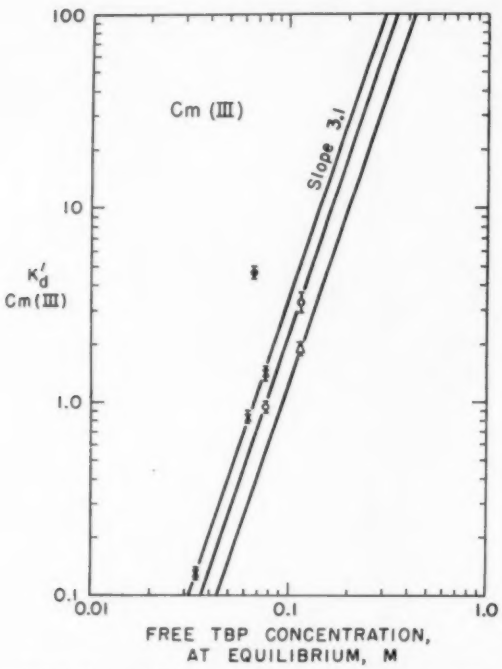


FIG. 6.—The distribution coefficients ($K_d'$) of Cm(III) as a function of free TBP concentration at equilibrium.
× pure nitrate melt. ○ nitrate melt containing 0·24 molal chloride ions.
Δ nitrate melt containing 0·43 molal chloride ions. Φ nitrate melt containing $NH_4NO_3$.

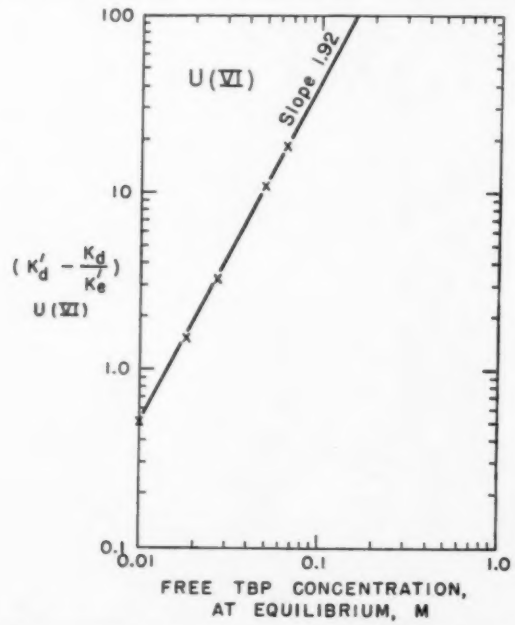


FIG. 7.—The corrected distribution coefficients ($K_d' - K_d/K_e'$) of U(VI) in a pure nitrate melt, as a function of free TBP concentration at equilibrium.

distribution coefficients, $k_d$ measured under these conditions were very low. Thus it was not possible to determine precisely the variation of the $k_k$'s as a function of the concentration of the extractant. Because of the higher values of the $K_d'$ in the fused nitrates this difficulty does not exist.

Figs. 1–6 for Li, Co, Nd, Eu, Am and Cm respectively, were obtained from equation (14) after having established graphically that $K_e[\text{TBP}]_o^q \gg 1$ in the following manner: assuming for each element a solvation number equal to the one obtained in aqueous systems a graph of $K_d'$ vs. $[\text{TBP}]_o^q$ was plotted. Owing to equation (12), it can be seen that the slope of the curve will be given by $K_dK_c/K_e'$ and that $K_d/K_e'$ will be equal to the value extrapolated to the origin. From these two ratios, $K_c$ can be calculated as well as $K_e[\text{TBP}]_o^q$. In each case, plotting log $K_d'$ vs. log $[\text{TBP}]_o^e$ yielded the same value for the solvation number as the one obtained in aqueous systems except for Co(II), where a solvation number of two had to be used to get agreement with the data. The same procedure was applied to uranium and as $K_e\,[\text{TBP}]_o^2$ was found to be of the order of magnitude of 1, equation (14) could not be used. Values of $q$ were found by plotting $\log\left(K_d' - \dfrac{K_d}{K_e'}\right)$ vs. $\log[\text{TBP}]_o^e$ where $K_d/K_e'$ was found in the same manner as described above (Fig. 7).

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## 5. *Separation factors for some actinide and lanthanide elements*

Table 6 gives the separation factors obtained for some lanthanide and actinide elements in pure nitrate melts and nitrate melts containing chloride ions. The

TABLE 6.—SEPARATION FACTORS (S.F.) FOR THE ACTINIDE AND LANTHANIDE ELEMENTS

| Elements | S.F. in a pure nitrate melt | S.F. in a nitrate-chloride melt (0·43 molal in chloride ions) |
|---|---|---|
| Eu(III)/Nd(III) | 3·8 | 4·5 |
| Eu(III)/Am(III) | 1·2 | 1·7 |
| Eu(III)/Cm(III) | 1·4 | 3·0 |
| Nd(III)/Am(III) | 1·2 | 1·7 |
| Cm(III)/Nd(III) | 2·6 | 1·4 |
| Cm(III)/Am(III) | 3·2 | 2·7 |

separation factor is defined as the ratio of the distribution coefficient of two elements and is therefore a measure of the extent of a separation between these elements. It can be seen from Table 6 that, with the exception of Cm(III)/Nd(III) and Cm(III)/Am(III) the separation factors are better in the system containing chloride ions than in the pure nitrate melt. The highest increase was found among those ratios involving Eu(III), the reason being that the distribution coefficients for Eu(III) were practically not affected by the presence of chloride ions although the distribution coefficients of all the other elements were markedly decreased.

For Cm(III)/Am(III), a separation factor of 3·2 is the best ever found in liquid–liquid extractions.

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# SYNERGIC EFFECTS IN THE SOLVENT EXTRACTION OF THE ACTINIDES—IV

## TRIVALENT PLUTONIUM, AMERICIUM AND EUROPIUM

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**Abstract**—By using radioactive tracers the solvent extraction of plutonium(III), americium(III) and europium(III) from 0·01 N hydrochloric acid, 0·001 N nitric acid, and an acetate buffer of pH 3·95 respectively into mixtures of 1,1,1-trifluoro-3-2′-thenoylacetone (TTA) and tri-*n*-butyl phosphate (TBP) in *cyclo*hexane has been studied. The extraction coefficient has been found to be greater for such mixtures than for either component alone and the extractable species has the composition $MX_3 \cdot 2TBP$ (where TTA = HX and M = Pu, Am, or Eu). This demonstrates the possibility of eight-fold co-ordination in these elements.

When the TBP is replaced by tri-*n*-butyl phosphine oxide (TBPO) a synergic enhancement of the extraction coefficient is again found. Here the TBPO replaces some of the chelating molecules and the species $MX_2(NO_3) \cdot 2TBPO$ and $MX_3$ (M = Am or Eu) appear to be co-extracted.

Some equilibrium constants are reported.

TRIVALENT actinides and lanthanides can be extracted into tributyl phosphate (TBP) from concentrated hydrochloric or nitric acids with distribution coefficients large and different enough to make separation possible. Trivalent metal complexes with 1,1,1-trifluoro-3-2′-thenoylacetone (TTA) are only extractable from aqueous solutions of low acidity, and the distribution coefficients for americium and for the rare earths (with the important exception of lanthanum) are so similar that separations are impracticable. Doubtless because of these limitations the solvent extraction of these elements with TTA has not been studied in any great detail.

WERNER and PERLMAN[1] have shown that americium(III) can be separated from lanthanum by using TTA, with an optimum separation factor at pH 3·3. The extraction of plutonium(III) into TTA has been studied by HEISIG and HICKS,[2] who experienced difficulty in preventing oxidation of the plutonium and noted that values of the distribution coefficient always increased on standing. The extraction of a trivalent ion by TTA may be represented by the equation

$$M^{3+}_{(aq)} + 3HX_{(o)} \rightleftharpoons MX_{3(o)} + 3H^{+}_{(aq)} \qquad (1)$$

for which the (mixed) equilibrium constant is defined by

$$\beta_{3,0} = [MX_3]_{(o)}[H^+]^3_{(aq)}/[M^{3+}]_{(aq)}[HX]^3_{(o)}.$$

Values for $\beta_{3,0}$ for some actinides and lanthanides are summarized in Table 1.

[1] WERNER and PERLMAN, Unpublished work quoted by HYDE, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 281. United Nations (1956).
[2] D. L. HEISIG and T. E. HICKS, U.S.A.E.C. Report UCRL-1664 (1952).

MCKAY and his co-workers[4] have shown that the species extracted by TBP from aqueous nitric acid has the composition $M(NO_3)_3 \cdot 3TBP$ (where M is a trivalent actinide or lanthanide).

CUNNINGHAME and his co-workers have already shown that the solvent extraction of praseodymium and neodymium by TTA is increased by the addition of TBP to the organic phase.[5] They interpreted their results by postulating the simultaneous extraction of mixed complexes such as $MX_2(NO_3) \cdot TBP$ and $MX(NO_3)_2 \cdot 2TBP$ with

TABLE 1.—MIXED EQUILIBRIUM CONSTANTS FOR THE EXTRACTION OF TRIVALENT ACTINIDES AND LANTHANIDES

| Lanthanides | | | Actinides | | |
|---|---|---|---|---|---|
| Metal | $\beta_{3,0}$ | Medium | Metal | $\beta_{3,0}$ | Medium |
| La | $2{\cdot}0 \times 10^{-10}$ | $HNO_3 + NaNO_3$ | Ac | $8{\cdot}0 \times 10^{-13}$ | |
| Ce | $1{\cdot}2 \times 10^{-8}$ | $HCl + NaCl$ | Pu | $2{\cdot}0 \times 10^{-5}$ | HCl* |
| Pr | $3{\cdot}3 \times 10^{-9}$ | $HCl + NH_4Cl$ | | $6{\cdot}0 \times 10^{-8}$ | |
| Nd | $7{\cdot}0 \times 10^{-9}$ | $HNO_3 + NaNO_3$ | Am | $2{\cdot}3 \times 10^{-9}$ | |
| Eu | $2{\cdot}2 \times 10^{-8}$ | $HCl + NaAc$[a] | | | |

* Present work. Other data from ref. (3).

the known complex species $MX_3$ and $M(NO_3)_3 \cdot 3TBP$. These results are at variance with the predictions we have made previously.[6] In all these species the co-ordination number is six. If, as seems likely, it can increase to eight, the synergic effect would arise as predicted in Part I of this series[6] by the addition of TBP to the tris-complex $MX_3$ rather than by replacement of one or more molecules of the chelating agent. It was therefore decided to investigate the solvent extraction of another rare-earth element into mixtures of TTA and TBP. Europium was chosen since its position in the $4f$ series is comparable with that of americium in the $5f$ series, and it was our intention to study this trivalent actinide and plutonium(III) as well.

## EXPERIMENTAL

The preparation of the extracting reagents and the procedure for carrying out equilibrations has already been described.[6]

A sample of "Spekpure" europium oxide (50 mg) was irradiated in the Harwell pile B.E.P.O. and after leaving for several days for short lived activity to decay it was dissolved in concentrated hydrochloric acid and taken to dryness. The process was repeated twice and the residue was then dissolved in concentrated nitric acid and taken to dryness: this was repeated twice more. The residue was finally dissolved in 0·5 N nitric acid and made up to 100 ml with the same acid. For equilibrations the stock solution was diluted twenty-fold, and 50 $\mu$l were used in each partition experiment in a total volume of 2 ml (concentration $\sim 4 \times 10^{-6}$ M) of a sodium acetate–hydrochloric acid buffer of pH 3·95. The activity of the $^{152}$Eu and $^{154}$Eu ($t_{\frac{1}{2}} = 13$ and 16 years) was determined with a scintillation counter.

The preparation of a stock solution of plutonium(III) presented some difficulty, since reducing agents commonly used in its preparation, e.g. hydroxylamine, will react with TTA. Reduction of a solution of Pu(IV) in concentrated hydrochloric acid with ammonium iodide, followed by passage through an anion exchange column to remove iodine and elution with concentrated hydrochloric acid gave a solution of plutonium(III), but it oxidized readily on being diluted, despite the presence of iodide ions. In the procedure finally adopted plutonium(IV) (20 mg) in nitric acid was treated with

[3] T. E. HICKS, B. RUBIN and T. VERMEULEN, U.S.A.E.C. Report UCRL-400 (1949).
[4] G. F. BEST, E. HESFORD and H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* **12**, 136 (1959).
[5] J. G. CUNNINGHAME, P. SCARGILL and H. H. WILLIS, AERE/C/M 215 (1954).
[6] H. IRVING and D. N. EDGINGTON, *J. Inorg. Nucl. Chem.* **15**, 158 (1960); cf. *Proc. Chem. Soc.*, 1959, 360.

ammonia and the dark green precipitate was centrifuged, washed, and taken up in concentrated hydrochloric acid. The solution was diluted to ~2N, warmed to decompose any polymeric Pu(IV), and passed down a Jones reductor containing lead shot pre-treated with 6 N hydrochloric acid and washed free from excess acid. The eluted Pu(III) was collected in a solution of ferrous sulphamate as a holding reductant. The stock solution in 0·01 N hydrochloric acid containing $10^{-3}$ M ferrous iron was passed through the Jones reductor daily to ensure that the plutonium(III) was fully reduced and in a reducing medium. Its purity was checked spectrophotometrically.[7] Aliquot portions for partition experiments were diluted to 2 ml with 0·01 N hydrochloric acid whereupon $[PuO^{3+}] \sim 5 \times 10^{-5}$ M.

## RESULTS AND DISCUSSION

Experimental results for the solvent extraction of europium from a buffer of pH 3·95 by mixtures of TTA and TBP in *cyclo*hexane are shown in Figs. 1 and 2. Fig. 1 shows the variation in log $q$ with variations in log [TBP] where the concentration of TTA is kept constant ([TTA] > [TBP] for series labelled 1,2,3 and 4; [TTA] < [TBP] for sets 5, 6 and 7). The lines of integral slope 2 establish the ratio [Eu]: [TBP] = 1: 2. Fig. 2 shows similar data for measurements in which [TBP] was constant and [TTA] was varied ([TTA] > [TBP] for sets 1,2,3 and 4; [TTA] < [TBP] for sets 5, 6 and 7). The lines here are drawn to an integral slope of three, thus establishing the composition of the extracted species as $EuX_3$,2TBP.

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Although these conclusions are in exact agreement with the predictions made in Part I[6] they disagree completely with the results obtained by CUNNINGHAME.[5] Here the evidence points to the formation of a single octa-co-ordinated species as being responsible for the synergic effect. CUNNINGHAME's experiments were interpreted on the basis of the co-extraction of $MX_3$, $MX_2(NO_3)\cdot TBP$, $MX(NO_3)_2\cdot 2TBP$ and $M(NO_3)_3.3TBP$ in all of which species a co-ordination number of six is preserved. The differences between the experimental results may be due to the much higher concentrations viz. 0·2M TTA and 1·2M TBP (30 per cent w/v) which he used. It is well known that ideal behaviour can only be assumed with concentrations of TTA up to 0·02 M and of TBP up to 0·05 M. At higher concentrations the distribution coefficients are always found to be lower than expected and the gradients of plots of the type shown in Figs. 1 and 2 would then progressively decrease with increasing concentrations of the reactants, leading to spuriously low values for the molar ratios of the components of the extractable complexes. Another consequence of the high concentration of TBP would be the increased interaction of the reagents, which would reduce the effective concentration of both, that of TTA being reduced to the greater extent.

Since the existence of the octa-co-ordinated species $EuX_3\cdot 2TBP$ has been established, the possibility of the *tris*-chelate $EuX_3$ having taken up water to form $EuX_3\cdot 2H_3O$ cannot be excluded although it has not been established experimentally. It is thus not possible at present to decide unequivocably between the addition reaction

$$MX_{3(o)} + 2TBP_{(o)} \rightleftharpoons MX_3\cdot 2TBP_{(o)} \qquad (2)$$

and the replacement reaction

$$MX_3\cdot 2H_2O_{(o)} + 2TBP_{(o)} \rightleftharpoons MX_2\cdot 2TBP_{(o)} + 2H_2O_{(o)} \qquad (3)$$

as the mechanism for the synergic effect.

It is, of course, possible that the co-ordination number remains at six for all the

[7] R. E. CONNICK, M. KASHA, W. H. MCVEY and G. E. SHELINE, *Radiochemical Studies: The Transuranium Elements* (Edited by C. D. CORYELL and N. SUGARMANN) NNES, Plutonium Project Record, Div. IV 14B p. 559. McGraw-Hill, New York (1949).

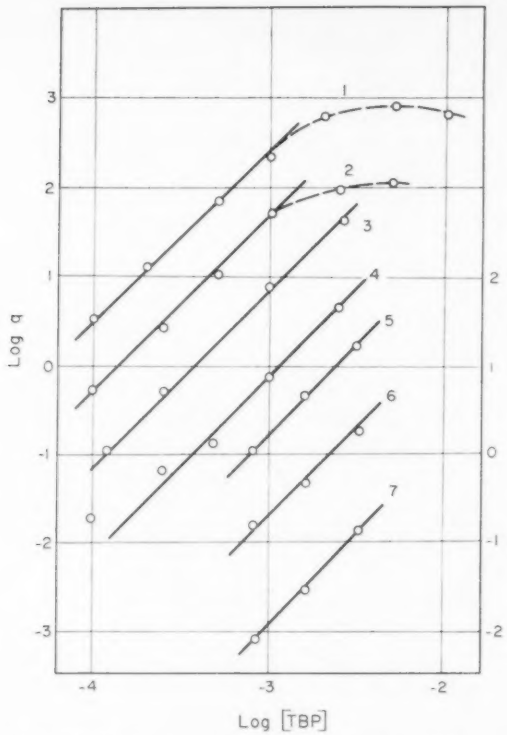


FIG. 1.—The variation in the distribution coefficient of europium(III) with increasing concentrations of TBP for fixed concentrations of TTA. (a) Set 1–4, left-hand ordinates, [TTA] > [TBP]. Curve 1. 0·02; Curve 2. 0·01; Curve 3. 0·005; Curve 4. 0·002 M TTA. (b) Set 5–7, right-hand ordinates, [TTA] < [TBP]. Curve 5. $1 \times 10^{-3}$; Curve 6. $5 \times 10^{-4}$; Curve 7. $2 \times 10^{-4}$ M TTA.

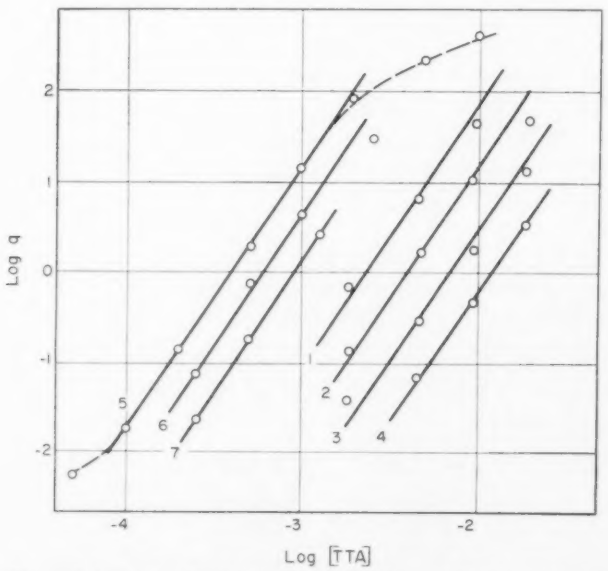


FIG. 2.—The variation in the distribution coefficient of europium(III) with increasing concentrations of TTA for fixed concentrations of TBP. (a) Set 1–4, [TTA] > [TBP]. Curve 1. $1 \times 10^{-3}$; Curve 2. $5 \times 10^{-4}$; Curve 3. $2 \times 10^{-4}$. Curve 4. $1 \times 10^{-4}$ M TBP. (b) Set 5–7, [TTA] < [TBP]. Curve 5. 0·02; Curve 6. 0·01; Curve 7. 0·005 M TBP.

lanthanon complexes. Should this be the case it would be necessary to postulate in reaction (2) that the co-ordination of TBP is only accomplished by forcing two chelated molecules of TTA to act as monodentate ligands only, a process which would involve a considerable loss of chelation energy. The species $MX_3 \cdot 2H_2O$ of reaction (3) could be formulated as hexaco-ordinate on the same assumption. In our opinion this seems less likely than the postulated increase in co-ordination number to eight. It is hoped to obtain an unequivocable decision by X-ray crystallography.

For the overall reaction

$$M^{3+}_{(aq)} + 3HX_{(o)} + 2TBP_{(o)} \rightleftharpoons MX_3 \cdot 2TBP_{(o)} + 3H^{+}_{(aq)} \quad (4)$$

values of the (mixed) equilibrium constant defined by

$$\beta_{3,2} = [MX_3 \cdot 2TBP]_{(o)}[H^+]^3_{(aq)}/[M^{3+}]_{(aq)}[HX]^3_{(o)}[TBP]^2_{(o)}$$

were calculated for europium (M = Eu) from the data:
[TTA] = 0·02 M, pH = 3·95, $q$ = 0·012 whence $\beta_{3,0} = 2{\cdot}2 \times 10^{-8}$, and $\beta_{3,2} = 60$.

Results for the extraction of americium(III) from $10^{-3}$ M nitric acid into mixtures of TTA and TBP in *cyclo*hexane are shown in Figs. 3 and 4. The integral slope of two in Fig. 3 ([TTA] constant) and of three in Fig. 4 ([TBP] constant) establish the composition of the extracted species as $AmX_3 \cdot 2TBP$.

In the absence of TBP the extraction of americium(III) from $10^{-3}$ M nitric acid with 0·02 M TTA yields a distribution coefficient of $q$ = 0·0019, whence the (mixed) equilibrium constant for reaction (1) is given by $\beta_{3,0} = 2{\cdot}4 \times 10^{-7}$. From the experimental data the average value of the mixed equilibrium constant $\beta_{3,2}$ is found to be $2{\cdot}6 \times 10^3$. If the synergic effect is to be explained in terms of equation (2) with M = Am, its equilibrium constant, defined as

$$K'_{3,2} = [MX_3 \cdot 2TBP]_{(o)}[MX_3]_{(o)}[TBP]^2_{(o)} \quad (5)$$

will be given by $\log K'_{3,2} = \log \beta_{3,2} - \log \beta_{3,0} = 10{\cdot}0$.

Results for the variation of $\log q$ with log [TTA] and log [TBP] for Pu(III) are shown in Figs. 5 and 6 for mixtures in which [TTA] < [TBP]. The integral slopes of three and two respectively establish the composition of the extractable species as $PuX_3 \cdot 2TBP$. Much effort was expended in studying systems in which the concentration of the diketone was held at 0·02 M while the concentration of the TBP was varied from $10^{-4}$ M to 0·02 M. Here, where [TTA] > [TBP], the results were poorly reproducible even when a holding reductant (ferrous sulphamate) was included in the aqueous phase to ensure the permanency of the trivalent state. We have found no convincing explanation for this anomalous behaviour when the relative proportions of the two extractants are thus changed. From the experimental data we estimate the value $\log \beta_{3,0} = -4{\cdot}7$ which is in marked disagreement with HEISIG and HICK's value[2] of $\log \beta_{3,0} = -7{\cdot}22$.

The results obtained for the three trivalent ions, two actinides and one lanthanide, are summarized in Table 2.

HEISIG and HICK's value for $\beta_{3,0}$ is probably more reliable than ours, and if theirs is adopted the equilibrium constants found for the trivalent actinides follow the pattern already disclosed by the hexavalent actinides.[6] By assuming as in Part II of this series[8] that any changes in the partition coefficient of a metal complex caused by a

[8] H. IRVING and D. N. EDGINGTON, *J. Inorg. Nucl. Chem.* **20**, 314, (1961).

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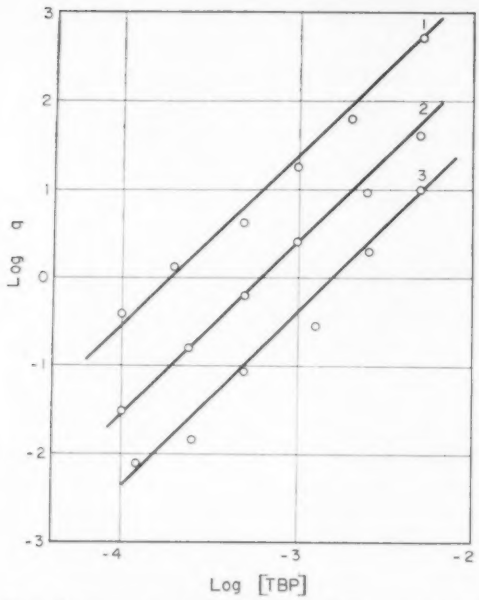


FIG. 3.—The effect of increasing concentrations of TBP on the distribution coefficient of americium(III) at fixed concentrations of TTA. Curve 1. 0·02; Curve 2. 0·01; Curve 3. 0·005 M TTA.

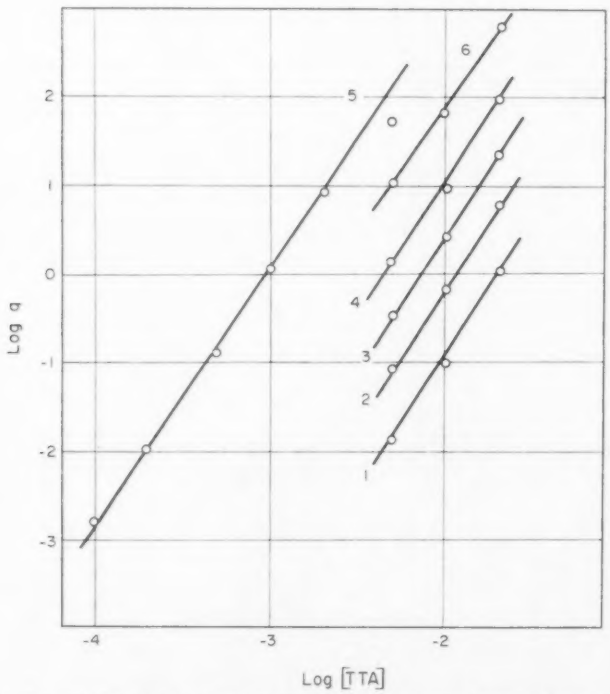


FIG. 4.—The variation in the distribution coefficient of americium(III) with increasing concentrations of TTA for fixed concentrations of TBP. (a) [TBP] < [TTA]. Curve 1. $2{\cdot}5 \times 10^{-4}$; Curve $2.5 \times 10^{-4}$; Curve 3. $1 \times 10^{-3}$; Curve 4. $2 \times 10^{-3}$; Curve 6. $5 \times 10^{-3}$ M TBP. (b) [TBP] > [TTA]. Curve 5. 0·02 M TBP.

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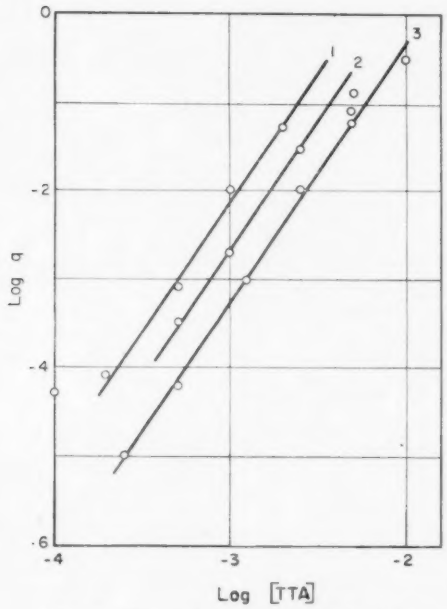


FIG. 5.—The variation in the distribution coefficient of plutonium(III) with increasing concentrations of TTA for fixed concentrations of TBP. Curve 1. 0·02; Curve 2. 0·01; Curve 3. 0·005 M TBP.

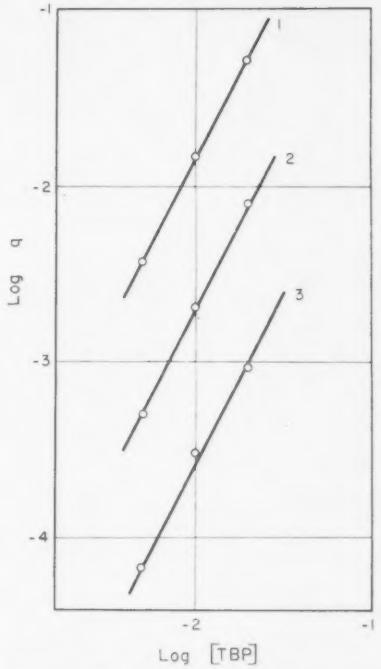


FIG. 6.—The variation in the distribution coefficient of plutonium(III) with increasing concentrations of TBP for fixed concentrations of TTA. ([TTA] < [TBP]). Curve 1. $2 \times 10^{-3}$; Curve 2. $1 \times 10^{-3}$; Curve 3. $5 \times 10^{-4}$ M TTA.

TABLE 2.—EQUILIBRIUM CONSTANTS FOR THE EXTRACTION OF TRIVALENT IONS BY MIXTURES OF TTA AND TBP

| | $\log \beta_{3,0}$ | $\log \beta_{3,2}$ | $\log K'_{3,2}$ |
|---|---|---|---|
| Europium | −7·66 | 1·78 | 9·44 |
| Americium | −6·62 | 3·41 | 10·03 |
| Plutonium | −4·70 | 5·30 | 10·0 |
| | −7·22[2] | — | 12·5* |

* Calculated from HEISIG and HICK's[2] value for $\log \beta_{3,0}$ and the present value for $\log \beta_{3,2}$.

change in the central ion to an ion of identical valency and similar ionic radius is of a lower order of magnitude than the corresponding changes in the stability constants of the respective complexes, it would appear from the values of $\beta_{3,0}$, $\beta_{3,2}$ and $K'_{3,2}$ that the effect of the actinide contraction is to favour the stability of $AmX_3$ compared with $PuX_3$. For this reason the replacement of any co-ordinated water, or the tendency to form adducts with TBP or TBPO, will decrease as the series is ascended, leading to $\beta_{3,2}(Pu) > \beta_{3,2}(Am)$, and to $K'_{3,2}(Pu) > K'_{3,2}(Am)$. The accuracy of the data is not high enough to justify any detailed discussion, but europium does appear to form a less stable *tris*-complex than either of the actinides and to show a lower tendency towards formation of an adduct.

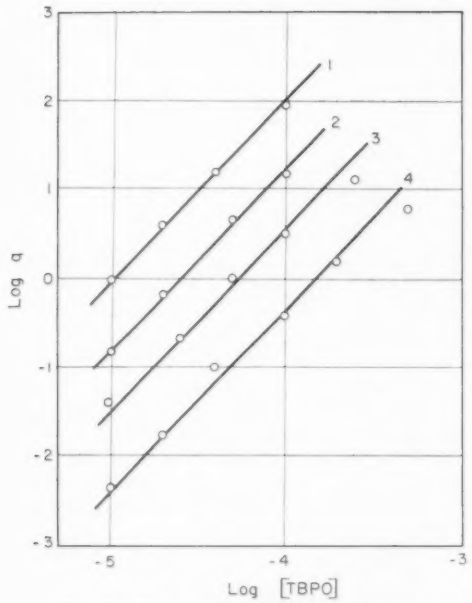


FIG. 7.—The variation in the distribution coefficient of americium(III) with increasing concentrations of TBPO for fixed concentrations of TTA. Curve 1. 0·02; Curve 2. 0·01; Curve 3. 0·005; Curve 4. 0·002 M TTA.

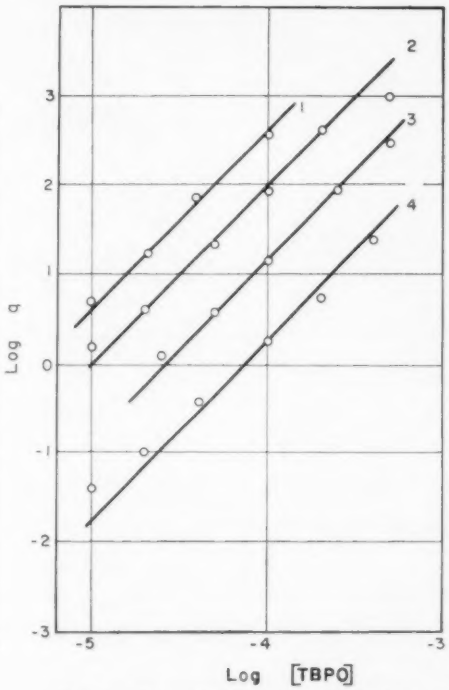


FIG. 8.—The variation in the distribution coefficient of americium(III) with increasing concentrations of TTA for fixed concentrations of TBPO. Curve 1. $1 \times 10^{-4}$; Curve 2. $5 \times 10^{-5}$; Curve 3. $2 \times 10^{-5}$; Curve 4. $1 \times 10^{-5}$ M TBPO.

In our previous studies of the solvent extraction of tetravalent actinides[8] we noted that the replacement of TBP by the more strongly donor solvent TBPO introduced a variety of complications, in that the phosphine oxide tended to replace chelated molecules of the diketone TTA to a greater or lesser extent. The same phenomena occur with the trivalent actinides and lanthanides studied here.

Figs. 7 and 9 show the variation in the values of log $q$ with log [TBPO] for constant concentrations of TTA, for the solvent extraction of americium(III) from $10^{-3}$ M nitric acid (Fig. 7) and of europium(III) from an aqueous buffer of pH 3·95 (Fig. 9). As before, *cyclo*hexane was used as the inert dilutent. The continuous lines are of integral slope 2.

Figs. 8 and 10 show corresponding plots of data for the variation in log $q$ with log [TTA] for fixed concentrations of TBPO. Here the best straight lines shown are of constant slope 2·4. From these results it is clear that any of the species extracted must contain two molecules of TBPO per atom of metal; but the fractional slope of 2·4 found in Figs. 8 and 10 implies that the *tris*-complex $MX^3$ must be co-extracted with complex species containing a lower proportion of diketone, e.g. $MX_2(NO_3)\cdot 2TBPO$ or $MX(NO_3)_2\cdot 2TBPO$.

Since the dependence of log $q$ on log [TBPO] is second-order, the participation of species such as $MX_2(NO_3)\cdot TBPO$ or $MX_3\cdot TBPO$ cannot be very important.

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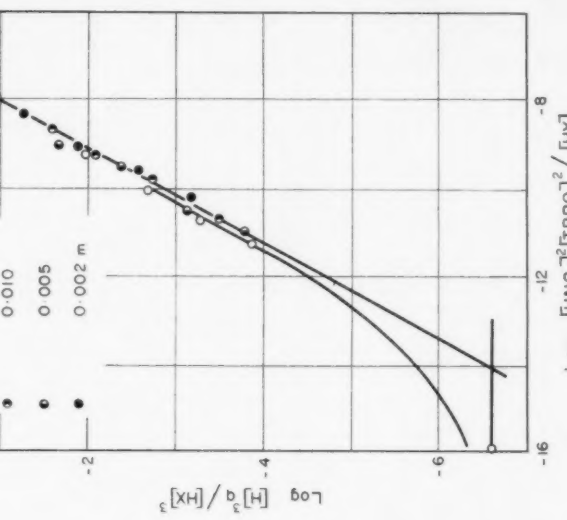



FIG. 11.—A graphical test of equation (8) for the solvent extraction of americium(III) by mixtures of TTA and TBPO and the evaluation of the constants $\beta_{3\cdot0}$ and $\beta_{2\cdot2}$.

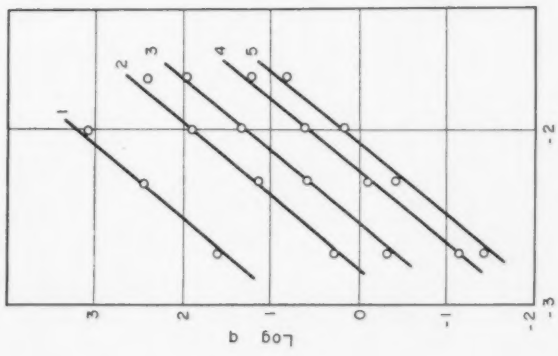



FIG. 10.—The variation in the distribution coefficient of europium(III) with increasing concentrations of TBPO for fixed concentrations of TTA. Curve 1. $5 \times 10^{-4}$; Curve 2. $1 \times 10^{-4}$; Curve 3. $5 \times 10^{-5}$; Curve 4. $2 \times 10^{-5}$; Curve 5. $1 \times 10^{-5}$ M TBPO.

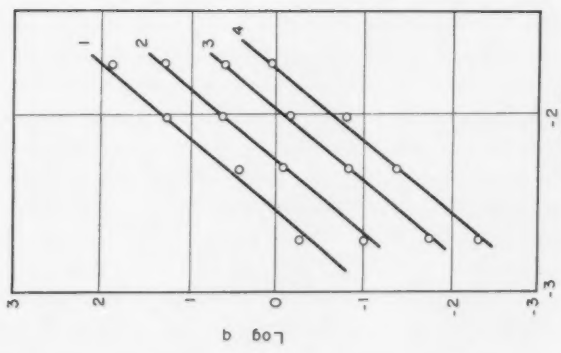



FIG. 9.—The variation in the distribution coefficient of europium(III) with increasing concentrations of TBPO for fixed concentrations of TTA. Curve 1. 0·02; Curve 2. 0·01; Curve 3. 0·005; Curve 4. 0·002 M TTA.

If $MX_3$ and $MX_2(NO_3)\cdot 2TBPO$ are the main extractable species we have

$$q = \{[MX_3]_{(o)} + [MX_2(NO_3)\cdot 2TBPO]_{(o)}\}/[M^{3+}]_{(aq)}$$

$$= \beta_{3,0}\frac{[HX]^3_{(o)}}{[H^+]^3_{(aq)}} + \beta_{2,2}\frac{[HX]^2_{(o)}[HNO_3]_{(aq)}[TBPO]^2_{(o)}}{[H^+]^3_{(aq)}} \quad (6)$$

where

$$\beta_{2,2} = \frac{[MX_2(NO_3)\cdot 2TBPO]_{(o)}[H^+]^3_{(aq)}}{[M^{3+}]_{(aq)}[HX]^2_{(o)}[HNO_3]^2_{(aq)}[TBPO]^2_{(o)}} \quad (7)$$

Equation (6) can readily be rearranged in the form $Y = 1 + X$, viz.

$$\frac{q[H^+]^3_{(aq)}}{\beta_{3,0}[HX]^3_{(o)}} = 1 + \frac{\beta_{2,2}[HNO_3]^2_{(aq)}[TBPO]^2}{\beta_{3,0}[HX]} \quad (8)$$

Fig. 11 is a plot of the experimental data in the form of a graph of $\log q[H^{3+}]/[HX]^3$ against $\log [HNO_3]^2[TBPO]^2/[HX]$. Its form supports the above hypothesis, and from the intersection of the asymptote with the ordinate axis we deduce that $\log \beta_{3,0} = -6{\cdot}60$. The point of intersection of the asymptotes occurs[8,9] where $\log \beta_{3,0} - \log \beta_{2,2} = -14{\cdot}0$, whence $\log \beta_{2,2} = 7{\cdot}4$.

The possibility of the participation of a mixed complex containing a still smaller proportion of TTA was considered. If $MX_3$ and $MX(NO_3)_2\cdot 2TBPO$ are the two species which are co-extracted, we would expect, by similar reasoning, that

$$\frac{q[H^+]^3}{[HX]^3\cdot\beta_{3,0}} = 1 + \frac{\beta_{1,2}[HNO_3]^2[TBPO]^2}{\beta_{3,0}[HX]^2} \quad (9)$$

where

$$\beta_{1,2} = \frac{[MX(NO_3)_2\cdot 2TBPO]_{(o)}[H^+]^3_{(aq)}}{[M^{3+}]_{(aq)}[HX]_{(o)}[HNO_3]^2_{(o)}[TBPO]^2_{(o)}}$$

Fig. 12 shows that the plot of $\log q[H^+]^3/[HX]^3$ against $\log [HNO_3]^2[TBPO]^2/[HX]^2$ for the experimental data does not fall on a single curve of the form expected, so that the above hypothesis is invalid.

Fig. 13 shows a similar treatment of the data from measurements of the solvent extraction of europium(III) from an aqueous buffer of pH 3·95 by mixtures of TBPO and TTA, on the assumption that $EuX_3$ and $EuX_2(NO_3)\cdot 2TBPO$ are the principal species extracted. This hypothesis is confirmed, and we deduce that $\log \beta_{3,0} = -8{\cdot}80$ and that $\log \beta_{3,0} - \log \beta_{2,2} = -14{\cdot}8$, whence $\log \beta_{2,2} = 6{\cdot}0$. When values of $q$ were calculated from equation (6) using the values of the equilibrium constants obtained in this way, agreement with the experimental results was quite satisfactory.

In reviewing the information obtained above on the composition of the mixed species responsible for the synergic enhancement of solvent extraction, one is struck by the fact that two molecules of TBP can be associated with the formation of an octa-co-ordinated complex $MX_3\cdot 2TBP$ with trivalent europium, plutonium or americium, whereas the co-ordination of two molecules of TBPO invariably causes the displacement of one a molecule of TTA. This is undoubtedly due to steric factors. If the complex $MX_3$ is initially hexa-co-ordinated as shown diagrammatically in Fig. 14(a) (where the broken lines represent the bidentate group from the diketone), the

[9] D. DYRSSEN. *Acta Chem. Scand.* **11**, 1771 (1957); D. DYRSSEN and L. KUČA, *ibid.*, **14**, 1945 (1960).

formation of an octa-co-ordinated molecule can occur through the intrusion of two donor molecules (represented as solid circles in Figs. 14(a) and 14(b)). By the use of scale models it can be shown that two molecules of TBP can be introduced into a tris-chelate of TTA and a trivalent ion without much difficulty. However, while there is a sufficient "gap" for the co-ordination of one molecule of TBPO, co-ordination of a second molecule is sterically hindered by the proximity of portions of the bidentate TTA, which must therefore be displaced if energy considerations are favourable.

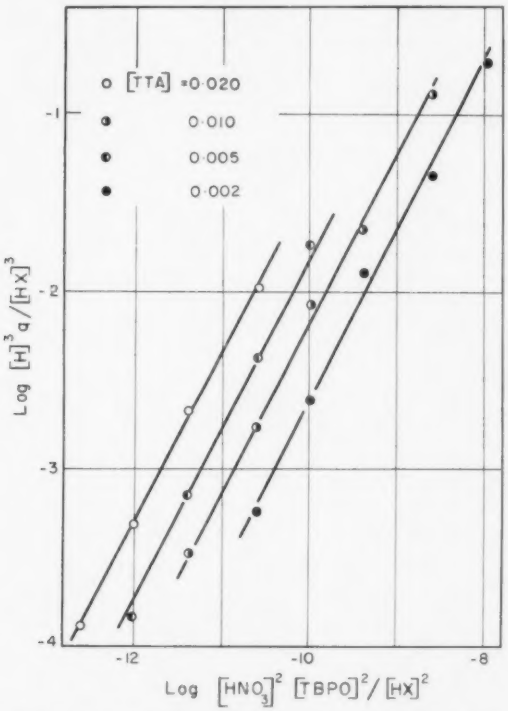



FIG. 12.—A graphical test of equation (9) for the solvent extraction of americium(III) showing that the species $MX(NO_3)_2 \cdot 2TBPO$ and $MX_3$ are not co-extracted.

By means of infra-red measurements on a Nujol mull of the tris-complex of TTA with praeseodymium we have recently confirmed[10] the presence of co-ordinated water. It may well be that all actinide and lanthanide complexes of TTA of the type $MX_3$ can accept water and achieve a co-ordination number of eight: if this proves to be the case the action of TBP to form the extractable species $MX_3 \cdot 2TBP$ is simply one of replacing one type of monodentate ligand by another of greater donor capacity while still retaining octa-co-ordination. If the nitrate ion enters as a monodentate ligand the co-ordination number of a mixed species such as $MX_2(NO_3) \cdot 2TBPO$ would appear formally to be seven—unless it also contains one molecule of water: this would not, of course, be disclosed by the method of experimentation employed in this paper. If, however, the nitrate ion acts as a bidentate ligand (as e.g. in the ion $[UO_2(NO_3)_3^-]$), octa-co-ordination is retained.

[10] H. IRVING and D. N. EDGINGTON. Unpublished observations.

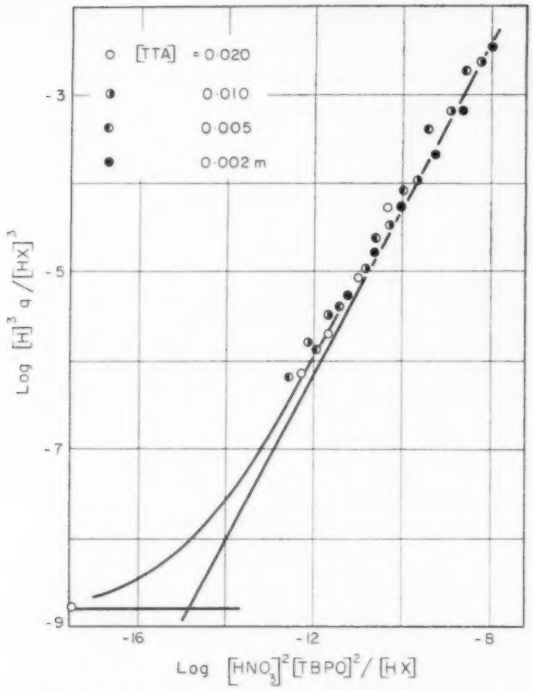
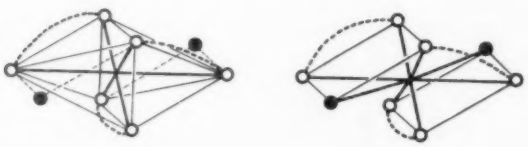



FIG. 13.—A graphical test of equation (8) for the solvent extraction of europium(III) and evaluation of the constants $\beta_{3,0}$ and $\beta_{2,2}$.



(a) (b)

FIG. 14.—Formation of an octa-co-ordinated adduct by the addition of two monodentate ligands (solid circles) to an octahedral complex (C.N. 6) formed by a *tris*-complex of a metal with a bidentate ligand (represented by broken lines).

If the metal in the complex $MX_2(NO_3)\cdot 2TBPO$ exhibits a maximum co-ordination number of six only it is necessary to postulate that the two chelate rings formed by the molecules of TTA have been forced open and that the loss of chelation energy has been compensated by the co-ordination of a bidentate nitrate group, two monodentate TBP molecules, and two molecules of TTA each acting only as monodentate ligands (cf. page 173).

*Acknowledgements*—We are indebted to the United Kingdom Atomic Energy Authority (A.E.R.E. Harwell) for financial support and for the generous loan of equipment. We should also like to thank Dr. E. GLUEKAUF for helpful discussions and assistance in very many ways. One of us (D. N. E.) is especially grateful to Dr. K. W. BAGNALL, Mr. N. JACKSON, and other members of the Chemistry Division, A.E.R.E. Harwell for their advice and friendly co-operation.

J. Inorg. Nucl. Chem., 1961, Vol. 21, pp. 181 to 189. Pergamon Press Ltd. Printed in Northern Ireland

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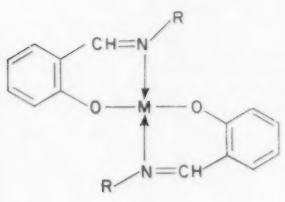
# NOTES

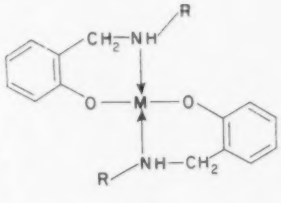
## Preparation and heat stability of a hydrogenated Schiff base chelate

(*Received* 16 *March* 1961)

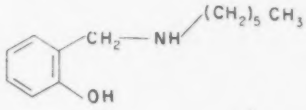
There has been recent interest in metal chelate compounds as possible heat stable materials, both in their own right,[1] and as part of the structure of heat stable metal-organic polymers.[2,3] Previous work in this laboratory has concerned the preparation[1,4] and heat stabilities[1] of the copper, nickel, and zinc Schiff base chelates I (R = an *n*-alkyl group).



I



II



III

Ia: R=n—$C_6H_{13}$, M=Zn  IIa: R=n—$C_6H_{13}$, M=Zn

It has seemed of interest to compare the properties, and in particular the heat stabilities, of the closely analogous metal chelates II. The compounds II can be considered to be formed by means of the hydrogenation of the two C=N bonds in I. No member of the series II appears to have been previously synthesized. We now wish to report the preparation of one such chelate, the zinc chelate of N-(*n*-hexyl)-*o*-hydroxybenzylamine (II*a*). We also report here the results of a comparison of the heat stability of II*a* with that of the corresponding Schiff base chelate I*a*.

Catalytic hydrogenation in ethanol of the Schiff base N-(*n*-hexyl) salicylaldimine readily yields the previously unreported secondary amine N-(*n*-hexyl)-*o*-hydroxybenzylamine (III). The latter compound is too heat sensitive to be vacuum distilled; attempts to do so lead to resin formation. This is in contrast with the corresponding Schiff base, N-(*n*-hexyl) salicylaldimine. The latter compound is readily purified by vacuum distillation. III can be obtained relatively pure simply by evaporating the filtered reaction mixture. The structure of III is evident from the $H_2$ consumption, the elemental analyses, the presence in the infra-red spectrum of an N–H stretching absorption peak and the absence of one due to C=N stretching.

Reaction of III with zinc acetate in methanol–water solution yields the zinc chelate II*a* which can be obtained in a beautifully crystalline form by recrystallization from methanol. Elemental analyses for the purified compound are in good agreement with the structure II*a*. Like the Schiff base chelate I*a*, compound II*a* has been obtained only in the anhydrous form. Also like I*a*, II*a* can be melted, but it melts over 100°C higher than does I*a*. Attempts to prepare the corresponding copper and nickel hexyl chelates II gave oily products which could not be purified adequately for characterization.

[1] R. G. Charles, *J. Inorg. Nucl. Chem.* **9**, 145 (1959).
[2] C. N. Kenney, *Chem. & Ind. (Rev.)* 880 (1960).
[3] D. B. Sowerby and L. F. Audrieth, *J. Chem. Educ.* **37**, 134 (1960).
[4] R. G. Charles, *J. Org. Chem.* **22**, 677 (1957).

Figure 1 shows the thermogravimetric curves obtained by heating the two zinc chelates I*a* and II*a* in an atmosphere of argon. II*a* began to lose weight rather abruptly, at about 250°C, somewhat above the melting point of the substance. Weight loss continued to 710°C, the highest temperature employed. The residue remaining in the sample container at 710°C was found to contain 99·6 per cent of the zinc initially present in the compound II*a* taken. This is conclusive evidence that the weight losses observed are due to volatilization of pyrolysis products rather than to evaporation of unchanged II*a*.

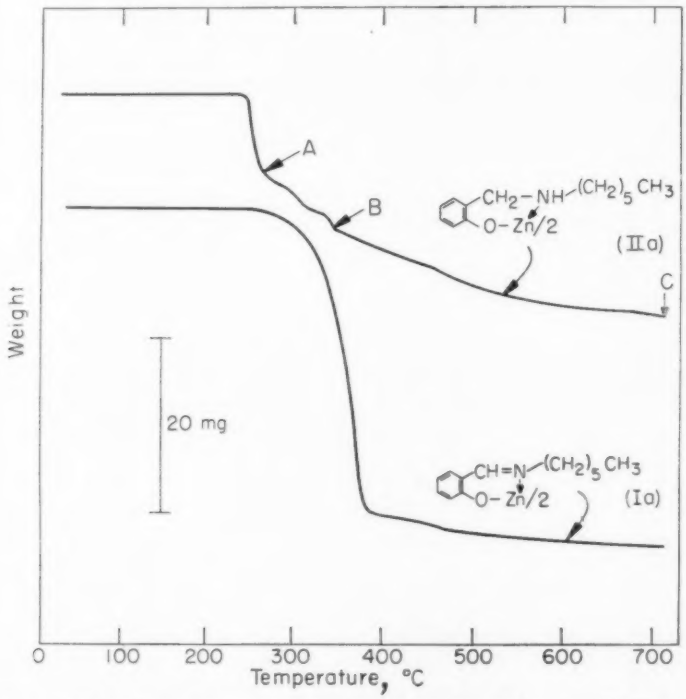



FIG. 1.—Weight loss–temperature curves for zinc chelates heated in argon. Fifty mg samples. The curves are displaced along the ordinate.

The thermogravimetric curve obtained for the Schiff base chelate I*a* shows a more gradual onset of weight loss which first becomes detectable at about 250°C. A white solid gradually condensed on the cool portions of the furnace tube. This material was identified as I*a* by its infra-red absorption spectrum. The residue remaining at 710°C contained only 50·2 per cent of the zinc present in the sample of I*a* taken. In a separate experiment I*a* was heated only to 310°C. The material remaining in the sample container had the same melting point as pure I*a*. These bits of evidence show that I*a* is not pyrolyzed at least to 310°C, under the conditions used, and that the initial weight losses for I*a* in Fig. 1 are due to evaporation of unchanged chelate. The compound I*a* is thus clearly more heat stable than is II*a*.

In separate experiments thermogravimetric curves were obtained for chelate II*a* which were terminated at the points A, B, and C shown in Fig. 1. Elemental analyses were determined for the residues obtained. The results are shown in Table 1. The initial decomposition of II*a* appears to involve the elimination of a fragment of composition $C_6H_{15}N$ (probably *n*-hexylamine). At higher temperatures the nitrogen content of the residue is further reduced and at 710°C the residue is nitrogen free. The residue at point A melted at 144–148°C and was soluble in toluene. The residues at B and C did not melt at 300°C. An X-ray powder pattern for the residue at C showed ZnO to be present as the only detectible crystalline component.

*Experimental*

*N*-(n-*hexyl*) *salicylaldimine*. Twelve and two tenths g (0·1 mole) of salicylaldehyde was mixed at room temperature with 11 g (an excess) of *n*-hexylamine. The mixture evolved heat spontaneously and water was given off. After the initial reaction subsided, the mixture was heated a few minutes on the hot plate. The mixture was cooled, dissolved in 50 ml of benzene, and extracted with three 100 ml

TABLE 1.—DECOMPOSITION RESIDUES FROM THE PYROLYSIS OF II*a* IN ARGON

| | Pyrolysis Temp. (°C) | Colour | %C | %H | %N | %O[a] | %Zn |
|---|---|---|---|---|---|---|---|
| A[b] | 265 | white | 62·9 | 6·4 | 3·8 | 9·8 | 17·3 |
| B | 340 | yellow | 60·1 | 5·4 | 2·5 | 12·1 | 19·9 |
| C | 710 | black | 62·6 | 1·9 | 0·0 | 8·0 | 27·5 |

*a*. By difference
*b*. Calculated for $C_{20}H_{25}NO_2Zn$: C, 63·75; H, 6·69; N, 3·72; O, 8·49; Zn, 17·35.

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portions of water. The latter were discarded. The benzene was distilled off and the residue was fractionally distilled *in vacuo*. The product was collected as a series of small fractions. Those fractions having the same index of refraction were combined and taken as the purified compound. Yield 82 per cent, based on the salicylaldehyde; b.p. 130–131°C at 2·2 mm-Hg; $n_D^{25}$ 1·5318; $d_4^{25}$ 0·9685. Analysis calculated for $C_{13}H_{19}ON$: C, 76·06; H, 9·33; N, 6·82. Found: C, 76·29; H, 9·31; N, 6·92. C=N infra-red stretching frequency at 6·13 $\mu$ (determination for the liquid).

bis-[*N*-(n-*hexyl*) *salicylaldimino*] *zinc*(II)

The preparation of this compound was described previously.[1] M.p. 92·5–93·5°C.

*N*-(n-*hexyl*)-o-*hydroxybenzylamine*

Fourteen and seven-tenths g (0·072 moles) N-(*n*-hexyl) salicylaldimine was dissolved in 150 ml absolute ethanol and 0·1 g $PtO_2$[5] added. The mixture was shaken at room temperature with $H_2$ at an initial pressure of 60 lbs/in.$^2$ for 1·75 hr in a Parr Pressure Reaction apparatus. The pressure decreased during the first 1·5 hr with over 90 per cent of the total pressure drop occurring during the first hour. The total hydrogen consumption, as determined by the pressure decrease, was 0·072 moles (theoretical 0·072 moles). The reaction mixture was filtered through sintered glass and the ethanol allowed to evaporate at room temperature. The residue was further dried in a vacuum desiccator. The residue consisted of 14·8 g of a light yellow oil. Analysis calculated for $C_{13}H_{21}ON$: C, 75·32; H, 10·21; N, 6·76. Found: C, 74·74; H, 10·13; N, 6·62. N–H stretching frequency at 3·03 $\mu$ (detn. for the liquid).

bis-[*N*-(n-*hexyl*)-o-*hydroxybenzylamino*] *zinc*(II)

N-(*n*-hexyl)-*o*-hydroxybenzylamine (2·28 g 0·011 moles) was dissolved in 25 ml methanol. Twenty-five ml of 0·20 M aqueous zinc acetate solution was added slowly while shaking the flask. A pale yellow flocculent precipitate separated during the addition. The mixture was stirred with a magnetic stirrer and 10 ml of 1·00 M aqueous KOH solution was added dropwise from a burette over a period of 0·5 hr. The mixture was cooled in the refrigerator and the solid collected by filtration. The product was dried in a vacuum oven for 2 hr at 100°C. Yield, 2·3 g. The crude chelate was purified by dissolving in 50 ml hot methanol followed by filtering through filter paper in a heated funnel. The cooled solution deposited delicate colourless needles. The purified product was collected by filtration and dried in the vacuum oven at 100°C. Yield 1·35 g; m.p. 221–222°C. Analyses calculated for $(C_{13}H_{20}NO)_2Zn$: C, 65·33; H, 8·44; N, 5·86; Zn, 13·68. Found: C, 66·5; H, 8·7; N, 5·9; Zn, 13·60.

[5] R. ADAMS, V. VOORHEES and R. L. SHRINER, *Organic Syntheses*, Collective Vol. I, Sec. Edition, J. Wiley & Sons, Inc., New York (1941). p. 463.

Attempts to prepare the corresponding copper(II) nickel(II) chelates by substituting the respective acetates in the above procedure gave very viscous brown (Cu) or green (Ni) oils which were not characterized.

*Heat Stability Studies*

Thermogravimetric curves were obtained with a recording thermobalance of the type previously described.[6] Fifty mg samples of the chelates were heated in a stream of argon (50 ml/min) at atmospheric pressure (ca. 730 mm-Hg). Temperature was raised linearly with time at 2·1°C/min.

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*Pittsburgh 35, Pennsylvania*

[6] R. G. CHARLES and A. LANGER, *J. Phys. Chem.* **63,** 603 (1959).

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## The ion exchange separation of *cis*- and *trans*- dichloro*bis*-(ethylenediamine) cobalt(III) nitrate.

(*Received* 7 *March* 1961; *in revised form* 29 *June* 1961)

The *bis*-(ethylenediamine) dichlorocobaltic nitrate complex $[Co(en)_2Cl_2]NO_3$, can exist in two stereoisomeric forms, *cis* and *trans*. It has been shown in several publications[1,2,3,4,5] that inert isomeric cationic octahedral complex ions can be separated by ion exchange.

In this paper the complete separation of the two cobaltic stereoisomers by means of cation exchange is described.

In spite of previous reports, a very short column (4 cm long) was used, which has the advantage of an easy cooling during the separation. We were obliged to do so because of the ready aquation of the two isomers at the ordinary temperature. The *cis* isomer aquates more, and the *trans* isomer less readily, the final product in each case is *cis*-$[Co(en)_2(H_2O)_2]^{3+}$.

### EXPERIMENTAL

The two isomers were prepared using the method of BAILAR[6]. The U.V.-visible spectra (Fig. 1) were taken dissolving the compounds in the least possible amount of water and diluting to the desired concentration with alcohol.[7]

A Hilger spectrophotometer was used for this purpose as well as for the determination of the two isomers during the separation.

In the latter case the *trans* isomer was determined at 6150 Å and the *cis* at 5350 Å. Because of the interference of the absorption of the two isomers when both were present in the same sample, two calibration lines were prepared for each isomer, the first at 6150 and the second at 5350 Å (Figs. 2 and 3).

The column (4 cm long and 1 cm dia.) was prepared with the strong cation exchange (Dowex 50w × 8, 100–200 Mesh) and was activated by successive treatments with 2 N HCl, water, 2 N NaOH and finally was used in the hydrogen form.

A number of preliminary experiments showed the best eluant to be a buffer solution of pH 5

[1] MOTOHICHI MORI, *et al. Nippon Kagaku Zasshi*, **76,** 1003–7, (1955).
[2] SVEN LINDENFORS, *Arkiv Kemi*, **10,** 561–8, (1957).
[3] JAHN T. HONGEN, *et al., J. Amer. Chem. Soc.*, **80,** 5015–8, (1958).
[4] P. GALLAGER, unpublished work Univ. Wisconsin.
[5] Inorganic Syntheses, Ed. by FERNELIUS, Vol. II. p. 222.
[6] M. L. ERNSBERGER and W. R. BRODE, *J. Amer. Chem. Soc.*, **56,** 1842–3 (1934).
[7] Modern Coordination Chemistry, J. LEWIS and R. G. WILKINS, p. 200, Interscience, New York, 1960.

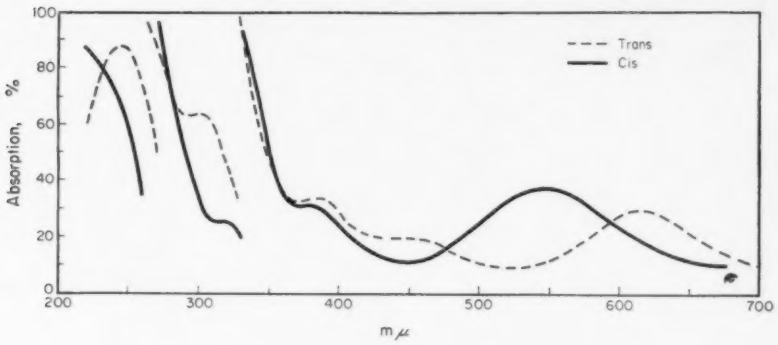


FIG. 1.

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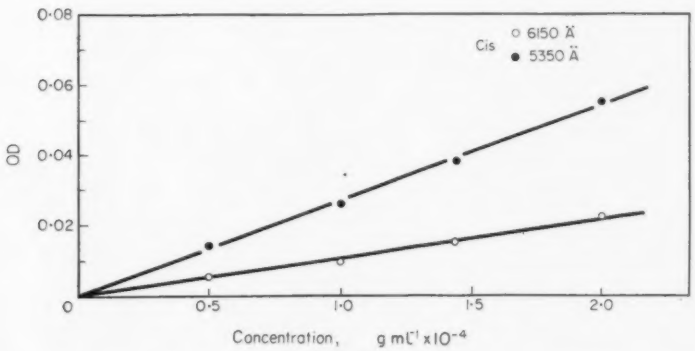


FIG. 2.

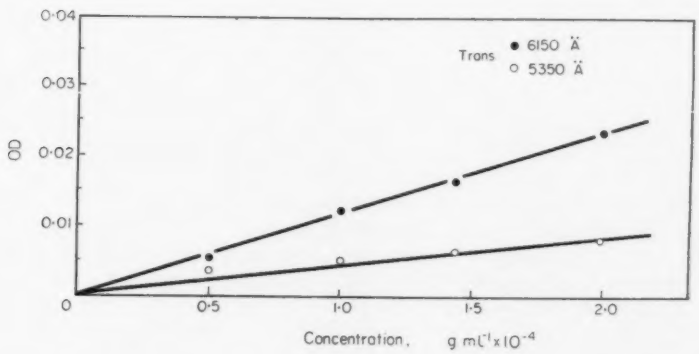


FIG. 3.

(mixture of phosphates and citric acid). In the present experiment, equal amounts of 0·05 g of each isomer were dissolved in water at a temperature of 15°C.

The solution was passed through the column during 45 min, while both isomers were adsorbed in the upper part of the column. The column was immersed in an ice-water bath during the separation.

The eluant was passed at a rate of 3 ml per 5 min. Portions of 3 ml of eluant were collected under the same conditions of cooling and the concentration of both isomers in each portion was determined immediately in order to avoid aquation. The time of the separation lasted 3 hr.

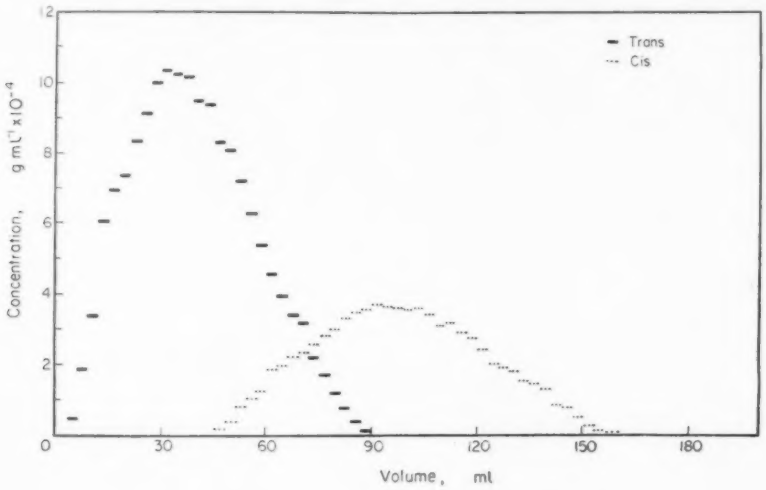


FIG. 4.

## RESULTS

The elution curves for the separation are shown in Fig. 4.

To determine the concentration of *trans*, $C_t$, and that of *cis*, $C_c$, in each sample in the presence of each other, the following equations were used.

$$C_t = \frac{A - B\dfrac{E_{c2}}{E_{c1}}}{E_{t2}\left(\dfrac{E_{t1}}{E_{t2}} - \dfrac{E_{c2}}{E_{c1}}\right)} \tag{1}$$

$$C_c = \frac{B - A\dfrac{E_{t2}}{E_{t1}}}{E_{c2}\left(\dfrac{E_{c1}}{E_{c2}} - \dfrac{E_{t2}}{E_{t1}}\right)} \tag{2}$$

where $A$ and $B$ are the measured optical densities of the sample at 6150 and 5350 Å respectively, $E_{t1}$, $E_{t2}$ the extinction coefficients of the *trans* isomer at 6150 and 5350 Å respectively and $E_{c1}$, $E_{c2}$ these of the *cis* isomer at the same wave lengths, taken from the calibration lines of Figs. 2 and 3.

From the experimental curves of Figs. 2 and 3 we obtain the values of $E_{t1}$, $E_{t2}$, $E_{c1}$, $E_{c2}$ which simplify the equations (1) and (2) to give

$$C_t = \frac{A - B\,0{,}4074}{82{,}92} \tag{3}$$

$$C_c = \frac{B - A\,0{,}3260}{234{,}13} \tag{4}$$

Hence by measuring in every mixture of *cis* and *trans* the total optical densities $A$ at 6150 and 5350 Å we have measured the concentration of each isomer.

## DISCUSSION

As was expected from all known cases, the *trans* form is more easily eluted because it is less polar and it is less strongly absorbed (8).

From graphical integration of the elution curves it is shown that 0·0478 g of *trans* and 0·0237 g of *cis* have been eluted from the column. This is due to the fact that a portion of *trans* (0·0022 g) and a portion of *cis* (0·0263 g) were transformed to the aquated form *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ during the adsorption time at 15°C temperature.

The aquated complex was adsorbed in the upper part of the column and did not move at all during the elution of the *cis* and *trans* isomers at pH 5.

This was easily eluted by more acid solutions.

*Acknowledgement*—One of the authors (P. D.) is indebted to Dr. A. G. Maddock, Radiochemistry Department, Lensfield Road, Cambridge, England, for helpful discussion.

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# Investigation of the changes in the oxidation number by the use of the $O^{18}$ isotope tracer techniques

(*Received* 25 *May* 1961; *in revised form* 2 *August* 1961)

In some earlier papers[1,2,3] we have described some changes in the oxidation number of different elements upon boiling in sulphuric acid. In the course of these experiments both oxidation and reduction processes have been observed, e.g. vanadium(V), chromium(VI), thallium(III), etc. upon boiling with sulphuric acid are partly or completely converted to a form of lower oxidation number. During these reactions an amount of oxygen corresponding to the extent of reduction is liberated.

To discover the nature of the reactions taking place we have performed some experiments using labelled sulphuric acid in a 77·7% w/w solution and enriched to 1·59 per cent in $O^{18}$. The oxygen liberated during the reduction was displaced into a glass bulb of about 50 ml. by a stream of oxygen-free nitrogen. The gas thus collected was analysed using a conventional analytical mass spectrometer to determine both its $O_2$ content and isotopic composition.

Previous data[4] on the exchange of $O^{18}$ records that the rate of the exchange reaction between permanganate or bichromate ions and water containing $O^{18}$ is very slow and in the case of the bichromate ions decreases with an increase in the acidity of the solution.

Using A.R. potassium dichromate and potassium permanganate the $O^{18}$ content of the oxygen liberated has been found to be the same as that of the labelled sulphuric acid, within the limits of the errors of the measurement, even if the time of the reaction did not exceed 4–5 min.

This result cannot be explained by a simple exchange mechanism. In our opinion the following explanation seems likely: in the presence of the bichromate or permanganate peroxydisulphuric acid is formed by the labelled sulphuric acid and subsequently rapidly and completely decomposes with evolution of oxygen. The $O^{18}$ content of the peroxydisulphuric acid is therefore reflected in the oxygen liberated. (It is known that the exchange between the peroxydisulphate ions and $H_2O^{18}$ in acidic medium is very slow (1–2 per cent) though it may be accelerated by increasing the pH of the solution.)[4] In addition it is known that decomposition of perdisulphate under these conditions

[1] E. Schulek, I. Pais and L. Pataki, *Annales Univ. Sci.* (*Budapest*), *Sect. chim.* **2**, 583 (1960).
[2] E. Schulek, L. Pataki and I. Pais, *Annales Univ. Sci.* (*Budapest*), *Sect. chim.* **2**, 587 (1960).
[3] E. Schulek, L. Pataki, L. Barcza and I. Pais, *Annales Univ. Sci.* (*Budapest*), *Sect. chim.* **2**, 593 (1960).
[4] A. I. Brodszkij: *Himija izotopov* (*Chemistry of the Isotopes*), *Moszkva, Tzdatelstvo Akad. Nauk. S.S.S.R.* 1957.

occurs without equilibration of the oxygen released with the water.[5] This hypothesis has been substantiated by experiments in which potassium peroxy-disulphate was boiled with labelled sulphuric acid. As was expected an exchange of less than 2 per cent between the sulphate and peroxy-disulphate ions was found.

Further experiments are planned to clarify these reactions.

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[5] M. DOLE, G. MUCHOW, DE F. P. RUDD and C. COMPTE, *J. Chem. Phys.* **20**, 961 (1952).

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## Preparation of fluoroborazines*

(*Received* 27 *July* 1961)

Diborane was found to react with tetrafluorohydrazine at 140° to 160°C to yield a mixture of fluoroborazines ($B_3N_3H_nF_{6-n}$) together with $BF_3$, $B_5H_9$, $H_2$, $N_2$, and $BF_3NH_3$. Reactions were carried out in sealed Pyrex bulbs at approximately 1/8 atm total pressure, using one-to-one mole mixtures and contact times of 15–30 min. Yields of fluoroborazines varied from 5–20 per cent. Preliminary separation of the reaction products was accomplished by high-vacuum fractional condensation techniques using traps at −63°, −78°, and −196°C.

A gas chromatographic apparatus was used to observe and separate components present in the −78° fraction. In place of a conventional chromatographic column a cold (−196°) copper tube was employed. The sample was introduced to the column in the helium carrier gas. The column was then gradually heated so as to produce a gradient decreasing in temperature from inlet to exit of the column. A thermal conductivity cell and recorder detected species as they successively evaporated from the thermal gradient column. A similar apparatus and its operation are described by CADY and SIEGWORTH.[1] As the components evaporated successively from the thermal gradient column, peaks corresponding to individual components were traced out by the recorder as in a chromatogram. Two fractions were collected, containing $B_3N_3H_5F$ and $B_3N_3H_4F_2$ respectively.

The mass spectrum of the $B_3N_3H_5F$ fraction was complex. The highest series of peaks began at a *m/e* of 92 and ended abruptly at 99. This latter peak (99) corresponds to the molecular weight of a $B_3N_3H_5F$ molecule containing three $B^{11}$ atoms. The remainder of the mass spectrum was complex from a *m/e* of 1 to 56 and showed two other groups of peaks, one at a *m/e* of 69 to 71 and the other at a *m/e* of 75 to 81. The infrared spectrum of this fraction was similar to that of borazole with sharp absorption maximums at 2·88 $\mu$ (N–H stretch), 3·96 $\mu$ (B–H stretch), 6·75 $\mu$ (B–F; very strong), 10·92 $\mu$, and 10·96 $\mu$. These latter two absorptions are in the region of N–F stretching. A number of other less intense absorptions were present in the region of 7–10 $\mu$ and in the region around 14 $\mu$.

The mass spectrum of the $B_3N_3H_4F_2$ fraction was similar to that of $B_3N_3H_5F$ with the exception of a series of peaks beginning at a *m/e* of 113 and ending abruptly at 117. This latter peak corresponds to the molecular weight of the $B_3N_3H_4F_2$ molecule containing three $B^{11}$ atoms. The infra-red spectrum of $B_3N_3H_4F_2$ was almost identical to that of $B_3N_3H_5F$. It differed only in the intensity and position of the weak bands between 7 $\mu$ and 10 $\mu$. Mass spectra of the less volatile fraction (−63°C) from the reaction indicated that $B_3N_3H_3F_3$ was also formed.

The authors believe that both the $B_3N_3H_5F$ fraction and the $B_3N_3H_4F_2$ fraction are mixtures of isomers. Although attempts to isolate the individual isomers were unsuccessful, the appearance of shoulders on the peaks in the chromatogram indicated that at least two species were present in each of the mono- and difluoroborazine fractions. It is apparent from consideration of the possible isomers that at least one N-substituted fluoroborazine was present in each of the fractions. Although it could be argued that one of the components in the $B_3N_3H_5F$ fraction was borazine, multiple components in the $B_3N_3H_4F_2$ fraction would support the presence of an N-substituted fluoroborazine.

* This work was performed under the auspices of the U.S. Atomic Energy Commission.

[1] G. H. CADY and D. P. SIEGWORTH, *Anal. Chem.* **31**, 618–20 (1959).

It is well to point out the hazards in working with this synthesis. Explosions were frequent while warming the sealed glass bulbs. These explosions invariably occurred a few seconds after removal of the reaction vessel from liquid nitrogen while still at very low temperatures. Once the reactants were in the gas phase at room temperature the mixture was stable, and no reaction occurred below the pyrolysis temperature of diborane. It is believed that detonation occurs in the liquid phase. It is recommended that the reactor be constructed so as to condense the $B_2H_6$ and $N_2F_4$ in separate compartments so that when warmed to room temperature their liquid phases do not mix.

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# BOOK REVIEWS

K. B. YATSIMIRSKII and V. P. VASIL'EV. Translated by D. A. PATTERSON. **Instability Constants of Complex Compounds**. viii + 218 pp. Pergamon Press Ltd., Oxford, 1960. 42s.

IT is difficult to know how to assess this book which consists of some 83 pages of descriptive material dealing with various theoretical and practical aspects of complex formation in solution followed by 120 pages of tables of stability constants. When it first appeared in Russian it was the first book in this field and the tables of data represented a considerable effort of compilation in that the literature was covered up to 1954 and partly to 1956. However the selection of data was somewhat arbitrary and the whole collection is now superseded by the comprehensive and authoritative tables published by the Chemical Society (Tables of Stability Constants Vol. I (Organic Ligands), Vol. II (Inorganic Ligands); *Chem. Soc. Special Publications No. 6 and 7*, 1957 and 1958).

The book ought therefore to be judged on the qualities of the earlier chapters. Chapter I (12 pages) outlines the mathematical conception of step-complex formation. Methods available for the experimental determination of step-constants are described in Chapter II under two main headings, viz. methods dependent upon solubility, distribution, ion-exchange, potentiometry and polarography, kinetic and "freezing methods", indicator, biological, and radioactive methods. The second group describes spectrophotometric, conductivity, cryoscopic and calorimetric methods. While these accounts will be of interest to the specialist they convey little information of the practical problems involved and emphasise insufficiently the factors which would cause one method to be preferred to another. Chapter III is devoted to a consideration of the thermodynamics of complex formation and Chapter IV, unquestionably the most valuable in this little monograph, is an interesting, if rather limited, account of factors determining the stability of complexes in solution which is specially significant for being the first review to have taken account of ligand field-theory and the effects of $\pi$-bonding.

The translation throughout is excellent and it is a matter for regret that this moderately priced book should not have appeared on the English market until the impact of its novelty had been dissipated by other works in this language.

H. IRVING

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M. STACEY, J. C. TATLOW and A. G. SHARPE: **Advances in Fluorine Chemistry**. 203 + vii pp. Butterworth's Publication, London, 1960. 45s.

*Musgrave*

This article contains a lot of useful information which is not embraced by the volume title, i.e. *ADVANCES* in Fluorine Chemistry and is more properly described as a review. The author could have been very much more economical in his text—terseness with clarity leads to a far more stimulating text as is readily seen if Sharpe's article is compared with Musgrave's. The latter reminds me somewhat of Mellor. The sections concerned with the preparations of halogen fluorides serve to give the newcomer to the field an adequate indication of the state of knowledge. However, those on the uses of fluoric halides in organic chemistry are rather disappointing in that vague process details are presented where scientific results are expected.

*Sharpe*

Sharpe's article starts off in good style and the reader is left in no doubt as to what he is in for in the way of a chemical "treat". The article deals factually, concisely and in a very readable manner with advances in the fluoride chemistry of transition metals which have taken place in the last decade.

He deals adequately with theoretical aspects of the crystalline state of these complexes, preparative methods and surveys of a wide range of compounds are presented in a well organized manner. This chapter provides very good reading for all students of inorganic chemistry, whether aged 18 or 80, and is a must for those with a particular interest in fluorides.

*Sharp*

Like Sharpe's article, this one is very adequately presented. Of the fluoroborates, the tetrafluoroborate receives the lion's share of attention, but of course, this only reflects on their relative stabilities as compared with tri- and di-fluoroborates. Physical constants, crystal considerations and thermodynamic properties receive their due acknowledgement. Reactions, formations and descriptions of a large number of inorganic, oxonium and carbonium tetrafluoroborates are presented. Again, a very strong recommendation as to the value of this article to the general and specialized reader.

*Burdon and Tatlow*

This article actually comprises more than the title suggests, since some (small) consideration is also given to the synthesis of inorganic fluorocompounds. Included are descriptions of apparatus, operating conditions and processes. The results of the latter are presented in a much more satisfactory manner than those of the first article and the reader feels that he is getting more scientific value for his money. Fluorination of a wide variety of compounds is considered. Whilst admitting that the electrochemical process is still an art in many respects, the authors nevertheless round off the article with a very useful discussion of possible mechanisms of this type of fluorination.

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*Stacey and Tatlow*

The type of fluorination described here is probably familiar to the general reader, most of whom will be aware, for instance, of the fluorinating potentialities of $CoF_3$ (c.f. $UF_6$ to $UF_4$ by $CCl_2$:CHCl). Whilst descriptions of apparatus, procedure etc. are in general satisfactory, it is surprising to find such an uninformative photograph (p. 171) included—line diagram with scale tells much more. Fluorination with $CoF_3$, $AgF_2$, $MnF_3$, $CeF_4$, $PbF_4$ are described; brief mention made of others, e.g. $UF_6$ (could quote here that the lower valency fluoride which is usually the by-product is here the main product). Again a useful discussion of possible mechanisms is included.

F. S. MARTIN

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# SOME NEUTRON-DEFICIENT ISOTOPES OF THULIUM AND ERBIUM

## A SURVEY OF HALF-LIVES AND $\gamma$-RAY SPECTRA WITH THE USE OF MASS-SEPARATED SAMPLES

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**Abstract**—Neutron-deficient isotopes of Tm and Er were produced in Er($p$, $xn$)-reactions. Chemical separation, as well as mass-separation of the products, was performed, and the half-lives and $\gamma$-ray spectra of the individual samples were measured. Definite mass assignments of the activities were made, and previously reported results essentially confirmed.

THE present paper reports on an attempt to provide more detailed information about the neutron-deficient isotopes of thulium and erbium.

The data existing before February 1958 on these nuclides is summarized in the Table of Isotopes.[1] Since then, the works of HARMATZ *et al.*[2] and JACOB *et al.*[3] have added considerable new information thereto. Although mass determinations by mass spectroscopy have been made on several Tm and Er isotopes,[4,5] mass assignments of some activities in this region are still uncertain.†

In this work we have performed chemical purification as well as isotope separation of thulium isotopes produced in Er($p$, $xn$) reactions with $x$ ranging from zero to 4 or 5. Each mass number has been characterized by its decay constants and $\gamma$-spectra.

### EXPERIMENTAL PROCEDURE

A more detailed description of the experimental procedure applied in this type of research has been published in an earlier paper.[9]

Two hundred and twenty milligrams of natural erbium oxide were irradiated for 5·5 hr with 65 MeV protons from the Uppsala synchro-cyclotron. Two to three milligrams of the target material were mass-separated in the electromagnetic isotope separator in Copenhagen. This set of samples, which was labelled "A-samples", was ready for counting 8 hr after termination of the bombardment. From ca. 30 mg of the target the thulium fraction was separated by cation-exchange chromatography.

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† After the conclusion of this work, research on the isotopes $^{164}$Tm and $^{162}$Tm[6] (1960) and $^{161}$Tm and $^{163}$Tm[7] and $^{163}$Ho[8] has been published.

[1] D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Rev. Mod. Phys.* **30,** 585 (1958).
[2] B. HARMATZ, T. H. HANDLEY and J. W. MIHELICH, *Phys. Rev.* **114,** 1082 (1959).
[3] K. P. JACOB, J. W. MIHELICH, B. HARMATZ and T. H. HANDLEY, *Phys. Rev.* **117,** 1102 (1960).
[4] M. C. MICHEL and D. H. TEMPLETON, *Phys. Rev.* **93,** 1422 (1954).
[5] D. R. NETHAWAY, M. C. MICHEL and W. E. NERVIK, *Phys. Rev.* **103,** 147 (1956).
[6] R. G. WILSON and M. L. POOL, *Phys. Rev.* **120,** 1827 (1960).
[7] F. D. S. BUTEMENT and P. GLENTWORTH, *J. Inorg. Nucl. Chem.* **15,** 205 (1960).
[8] R. A. NAUMAN, M. C. MICHEL and J. L. POWER, *J. Inorg. Nucl. Chem.* **15,** 195 (1960).
[9] K. S. TOTH, S. BJØRNHOLM, M. H. JØRGENSEN, O. B. NIELSEN, O. SKILBREID and A. SVANHEDEN, *J. Inorg. Nucl. Chem.* **14,** 1 (1960).

Subsequently this fraction was mass-separated. The mass-separated samples were labelled "B-samples" and were ready 11 hr after the bombardment.

A 3 × 3 in. NaI(Tl) scintillation crystal was used in connexion with a 256-channel analyser to record the $\gamma$-spectra of the two sets of samples. The decay of each mass number was followed, using a windowless, flow-type proportional counter operated on the $\beta$-plateau, as well as using a single-channel scintillation spectrometer with a 1 × 1 in. NaI(Tl)-crystal.

## RESULTS

The decay of each sample was followed for about four months. Fig. 1 shows the variation in the activities of the two series of samples, "A" and "B", with respect to mass number and time after termination of the bombardment. The values of the counting rates were taken from the flow-counter measurements, and corrected for general background only.

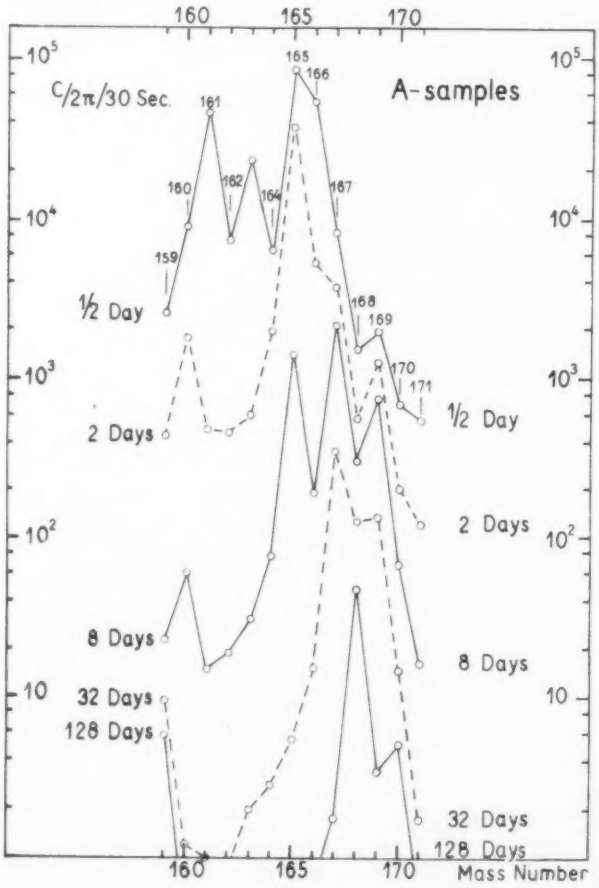


FIG. 1(a).

FIG. 1.—Radioactive decay of mass-separated samples. Part A shows the proton irradiated erbium oxide target resolved in mass numbers 159–171. Part B (next page) shows the thulium fraction of the same target resolved in the same mass numbers. Points representing activities measured simultaneously are connected with curves. Each curve is labelled with the time after termination of the bombardment. The time intervals between the curves increase with a factor of four.

The predominant reactions occurring in the erbium oxide target irradiated with 65 MeV protons are $(p, xn)$ reactions with $x = 3, 4$ and 5. The distribution of resultant activities versus mass number shown in Fig. 1 illustrates this fact, taking the abundances of stable erbium isotopes into consideration.

Every mass number showed a complex decay. Besides the activity of the proper mass number each sample contained background activities of different origin:

(1) Part of the radioactive material placed in the ion source of the isotope separator was almost uniformly distributed over the collector during the separation, thus giving rise to a "smear-out" activity having the same relative composition as the A- and B-samples before mass separation. The magnitude of the "smear-out" activity in a set of samples was about one per cent of the total activity in the set.

(2) In every sample corresponding to a given mass number a certain part of the activities of the two neighbouring mass numbers was found, usually a few per cent.

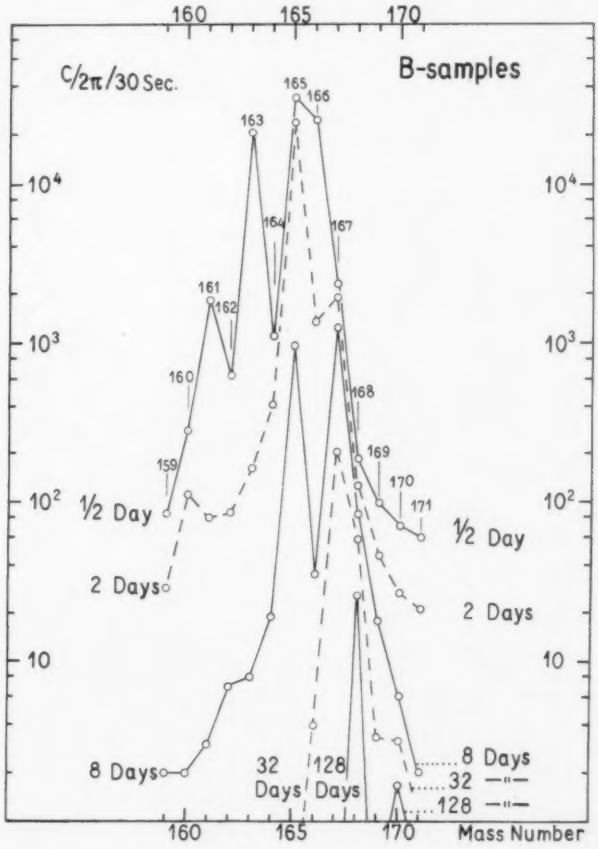


FIG. 1(b).

This contamination was due to the finite resolving power of the isotope separator, which generally yields a separation factor of the order of one hundred.

The efficiency of the chemical separation can be checked by means of the activity of mass number 169 in the two series, "A" and "B". $^{169}$Tm is stable; hence mass number 169 in the B-series should not display any activity when corrected for background

effects. However, an amount of $^{169}$Er was found to be present in the B-sample, too. Comparison between the relative amount of $^{169}$Er in the A- and B-samples yields a value of approximately twenty-five for the chemical purification factor.

A sample of the target taken out before mass separation was tested for $\alpha$-activity with the flow-counter operated on the $\alpha$-plateau. No $\alpha$-activity was detected, the ratio of $\alpha$- to $\beta$- counts being less than $10^{-5}$.

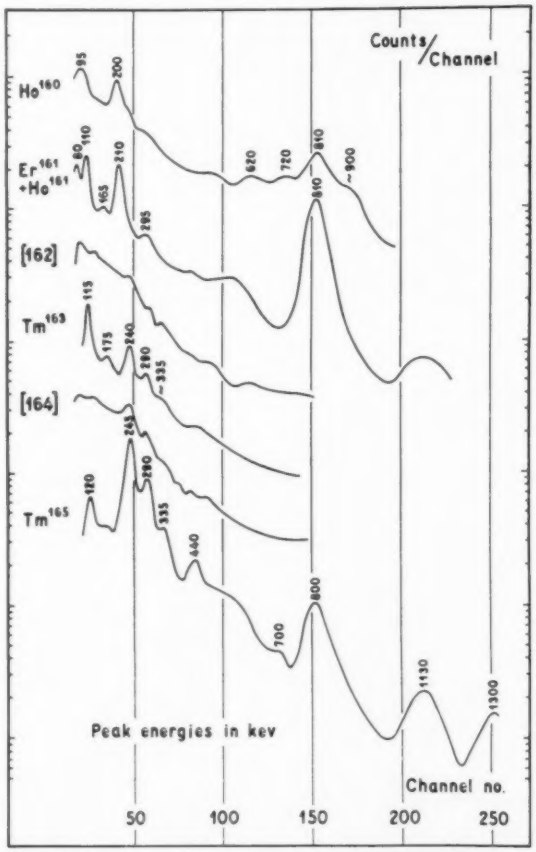


FIG. 2.—$\gamma$-spectra recorded 1–2 hr after mass separation with a 256 channel pulse-height analyser combined with a 3 × 3 in NaI(Tl)-crystal. The $\gamma$-spectra are placed arbitrarily with respect to the logarithmic scale indicated at the extreme right. By means of this scale the relative intensities of peaks within a particular spectrum can be judged. The statistics are so that the top of the highest peak of each spectrum corresponds to about 4000 counts/channel. Mass numbers 160 and 161 are taken from the A-samples (not chemically separated), whereas the mass numbers 162, 163, 164 and 165 are taken from the chemically separated thulium fraction (B-samples).*

Table 1 lists the half-lives of the nuclides belonging to a given mass number as determined from the corrected decay curves. Comparison between corresponding A-samples (not chemically separated) and B-samples (thulium fraction) provides element assignment for the thulium activities, but in general it is not possible to assign any atomic number to the daughter activities. However, daughter activities

* Note that unambiguous element assignments only can be made on masses 163 and 165. The $\gamma$-spectra of masses 162 and 164 are evidently due to contamination from other mass numbers.

TABLE 1.—HALF-LIVES

| Isotope | Sample A | | Sample B | | Weighted mean |
|---|---|---|---|---|---|
| | Flow-counter | $\gamma$-counter | Flow-counter | $\gamma$-counter | |
| ($^{159}$Dy) | 130 ± 20 days | | | | 130 ± 20 days |
| ($^{160}$Er) | 28·7 ± 0·5 hr | | | | 28·7 ± 0·5 hr |
| ($^{161}$Er) | 3·2 ± 0·1 hr | | 3·5 ± 0·3 hr | | 3·2 ± 0·1 hr |
| ($^{161}$Ho) | 1·9 ± 0·5 hr | | | | 1·9 ± 0·5 hr |
| $^{162}$Tm | <45 min | | | | <45 min |
| $^{163}$Tm | 1·8 ± 0·1 hr | 1·8 ± 0·1 hr | 1·8 ± 0·1 hr | 1·9 ± 0·1 hr | 1·8 ± 0·1 hr |
| ($^{163}$Er) | 1·0 ± 0·5 hr | 1·0 ± 0·5 hr | 1·0 ± 0·5 hr | | 1·0 ± 0·5 hr |
| $^{163}$Ho | | | >500 yr | | >500 yr |
| $^{164}$Tm | <45 min | | | | <45 min |
| $^{165}$Tm | 30·2 ± 0·1 hr | 29·9 ± 0·1 hr | | | 30·1 ± 0·1 hr |
| $^{165}$Er | | | 9·8 ± 0·5 hr | 9·1 ± 0·5 hr | 9·5 ± 0·5 hr |
| $^{166}$Tm | 8·0 ± 0·2 hr | 8·0 ± 0·2 hr | 7·8 ± 0·2 hr | 8·0 ± 0·2 hr | 8·0 ± 0·2 hr |
| $^{167}$Tm | 9·3 ± 0·1 days | 9·2 ± 0·2 days | 9·3 ± 0·1 days | 9·2 ± 0·2 days | 9·3 ± 0·1 days |
| $^{168}$Tm | 95 ± 10 days | | 95 ± 10 days | | 95 ± 10 days |
| $^{169}$Er | 9·6 ± 0·1 days | | | | 9·6 ± 0·1 days |

TABLE 2.—$\gamma$-RAY ENERGIES AND RELATIVE INTENSITIES

| Mass number | $E_\gamma$ (keV) | $I_\gamma$ | Element assignment | Reference |
|---|---|---|---|---|
| 161 | 80 | 4* | Ho | 2, 12 |
| | 110 | 5 | Ho | 2 |
| | 165 | 1 | Ho | 2, 12 |
| | 210 | 8 | Er | 2, 13 |
| | 295 | 2 | | |
| | 810 | 35 | Er | 13 |
| | 1120 | weak | Er | 13 |
| 163 | 115 | 8* | Tm | 2 |
| | 175 | 1 | Tm | 2 |
| | 240 | 5 | Tm | 2 |
| | 290 | 3 | Tm | 2 |
| | 335 | 3 | Tm | 2 |
| 165 | 120† | 5‡ | Tm | 2 |
| | 245 | 50 | Tm | 2 |
| | 290 | 35 | Tm | 2 |
| | 335 | 10 | Tm | 2 |
| | 440 | 5 | Tm | 2 |
| | 700 | 2 | Tm | 2 |
| | 800 | 15 | Tm | 2 |
| | 1130 | 5 | Tm | 2 |
| | 1300 | 1 | Tm | 2 |

* Intensities are given as per cent of total X-ray intensity.
† Part of the intensity could be due to the sum line of 2 K—X-rays.
‡ Intensities are given as per cent of the part of the X-ray intensity which was calculated to belong to the $^{165}$Tm decay.

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could in all cases be identified with previously reported isotopes of erbium, holmium or dysprosium. We have listed these isotopes in Table 1 with the symbols in parentheses.

Fig. 2 shows a series of $\gamma$-spectra recorded with the same setting of the scintillation spectrometer. The X-ray peaks have been left out. Table 2 lists the intensities of the photopeaks in per cent of the X-ray intensity for some of the nuclides. All intensities were corrected for crystal efficiency.

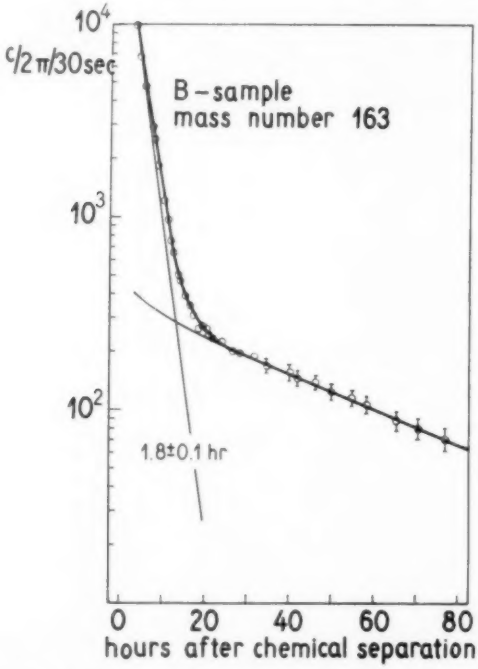


FIG. 3.—Decay of mass number 163 of the thulium fraction, recorded with a windowless flow-type proportional counter. The part of the curve with a small slope is due to "smear-out" activity, proportional to the total activity of the thulium fraction before mass separation. As such, it is extrapolated and subtracted from the gross decay curve. Remaining is a 1·8 ± 0·1 hr half-life belonging to $^{163}$Tm (in transient equilibrium with the $^{163}$Er daughter).

In the following each mass number is discussed separately.

*159.* The A-sample contained a 130 ± 20 days half-life, which can be ascribed to 144 days $^{159}$Dy.[10]

*160.* The A-sample decayed with a 28·7 ± 0·5 hr half-life. The $\gamma$-spectrum of this mass number showed peaks at 95 and 200 keV and some less pronounced lines at 620, 720 and 900 keV, besides the 810 keV peak due to contamination with mass number 161. NERVIK and SEABORG[11] have reported 29·4 hr $^{160}$Er to decay by pure *K*-capture with no $\gamma$-rays to 5·0 hr $^{160}$Ho, for which $\gamma$-rays of energies 87, 194, 650, 730, 890 and 970 keV were observed. This is consistent with our data for mass number 160, and we can thus assign the 28·7 hr half-life to $^{160}$Er and the $\gamma$-spectrum to $^{160}$Ho.

*161.* No Tm-activity was observed in the B-sample, whereas the A-sample showed

[10] B. H. KETELLE and A. R. BROSI, *Phys. Rev.* **116,** 98 (1959).
[11] W. E. NERVIK and G. T. SEABORG, *Phys. Rev.* **97,** 1092 (1955).

a 3·2 ± 0·1 hr half-life with indications of a 1·9 ± 0·5 hr daughter growing in. These two activities can be ascribed to $^{161}$Er and $^{161}$Ho, respectively. For this pair, half-lives of 183 min (3·1 hr)[11] and 2·5 hr[12] have been reported. The $\gamma$-spectrum of mass 161 is shown in Fig. 2 and Table 2. The assignment of the $\gamma$-lines can be made on the basis of literature only.[2,12,13] One line at 295 keV seems to be new.

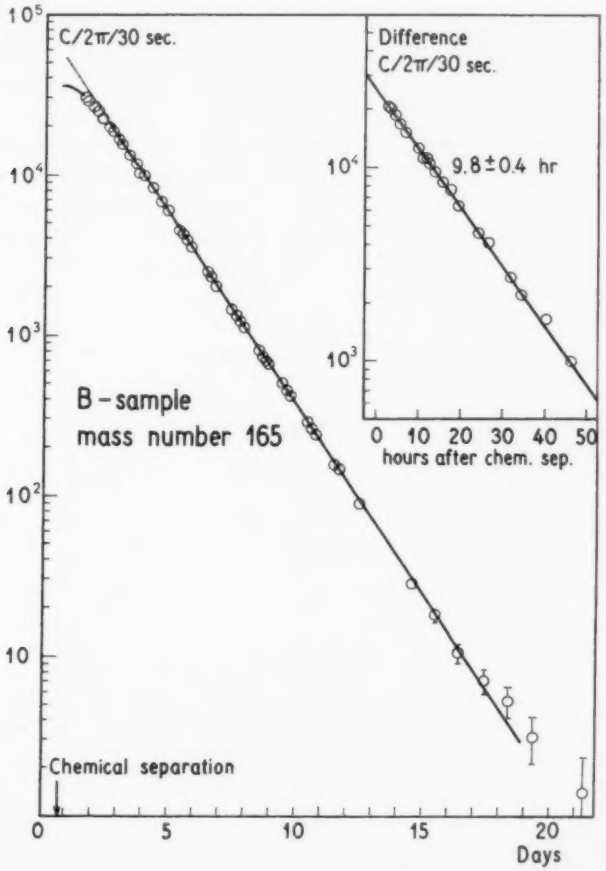


FIG. 4.—Decay of mass number 165 of the thulium fraction recorded with a windowless flow-type proportional counter. The high production yield of 30·1 hr $^{165}$Tm makes the background effects relatively less pronounced. The growth of the 9·8 ± 0·4 hr $^{165}$Er daughter is shown in the small insert.

*162.* The activity of this mass number was due solely to background from neighbouring mass numbers and "smear-out". $^{162}$Tm is probably shortlived. In this case, an upper limit of about 45 min can be put on the half-life, assuming $^{162}$Tm to have the same production rate in the cyclotron bombardment, and the same counting efficiency in the flow-counter, as $^{163}$Tm.

*163.* The half-life of $^{163}$Tm was found to be 1·8 ± 0·1 hr (see Fig. 3). Indications of a growth in activity with half-life of the order of one hour could be observed. A

[12] T. H. HANDLEY, *Phys. Rev.* **94**, 945 (1954).
[13] T. H. HANDLEY and E. L. OLSON, *Phys. Rev.* **93**, 524 (1954).

75 min half-life has been assigned to $^{163}$Er by HANDLEY and OLSON.[14] $^{163}$Er decays in turn to $^{163}$Ho. This nuclide is believed to possess a very long half-life. We are able to set a lower limit on the $^{163}$Ho half-life of roughly 500 years on the basis of the decay curves. All the $\gamma$-rays listed in Table 2 could be identified with the conversion lines reported for the $^{163}$Tm decay.[2] Several of the $\gamma$-rays appear to be double.

*164.* No $^{164}$Tm activity was detected. Using analogous arguments as in the case of $^{162}$Tm, we set an upper limit of approximately 45 min for the $^{164}$Tm half-life.

*165.* The decay curve of the B-sample is shown in Fig. 4. $30{\cdot}1 \pm 0{\cdot}1$ hr $^{165}$Tm, with a $9{\cdot}5 \pm 0{\cdot}5$ hr daughter growing in, was observed. The daughter activity is ascribed to $^{165}$Er. These two half-lives have previously been measured to be 29 hr[14] and $10{\cdot}0 \pm 0{\cdot}1$ hr,[15] respectively. Two $\gamma$-spectra of mass number 165, corresponding to different mixtures of $^{165}$Tm and $^{165}$Er, were recorded. All $\gamma$-rays maintain the same relative intensities, whereas the X-ray line in the sample most abundant in $^{165}$Er was more intense. We therefore assign all the $\gamma$-rays to the $^{165}$Tm-decay, although this procedure is subject to some uncertainty in the case of the weaker lines. The energies of the $\gamma$-rays agree well with the previously measured conversion line spectrum.

*166.* $^{166}$Tm decayed with an $8{\cdot}0 \pm 0{\cdot}2$ hr half-life. The decay was studied, using a six-gap $\beta$-spectrometer in connexion with coincidence measurements. This study will be published separately.

*167 and 168.* Half-lives of $9{\cdot}3 \pm 0{\cdot}1$ days and $95 \pm 10$ days were found for $^{167}$Tm and $^{168}$Tm, respectively.

*169.* The half-life of $^{169}$Er, present in the A-sample, was measured to be $9{\cdot}6 \pm 0{\cdot}1$ days.

[14] T. H. HANDLEY and E. L. OLSON, *Phys. Rev.* **92**, 1260 (1953).
[15] F. D. S. BUTEMENT, *Proc. Phys. Soc.* Lond. **63** A 775 (1950).

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# ISOMERIC CROSS-SECTION RATIO FOR THE ($\alpha$, $pn$) REACTION

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**Abstract**—Isomeric cross section ratios have been measured at $\alpha$-particle bombarding energies up to 40 MeV for the formation of $^{254}$Es isomers from $^{252}$Cf. The high-spin isomer was not observed, and a lower limit of 34 could be set for the cross-section ratio (low spin/high spin).

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A NUMBER of investigators[1,2,3] have studied the variation in the ratio of the cross-sections of isomeric states in nuclear reactions as a function of the bombarding energy. Since the difference in spins of such states is usually large, it is possible to attempt deductions about the effect of angular momentum on the nuclear reactions involved. VANDENBOSCH and HUIZENGA[4] have been able to correlate the experimental ratios for the production of the $^{197}$Hg isomeric pair by a variety of reactions likely to proceed via compound-nucleus formation, with ratios calculated by a statistical model in which the effect of angular momentum is considered. Low ratios in the ($\alpha$, $\alpha n$) and ($d$, $p$) reactions were interpreted as evidence of a direct-interaction mechanism for these reactions.

The ($\alpha$, $pn$) reaction has been studied by SILVA[5] for a wide range of targets from $^{60}$Ni to $^{238}$U. The ($\alpha$, $pn$) reaction in most cases was shown to proceed by prompt emission of a proton, followed by neutron evaporation. The relative contribution of the ($\alpha$, $d$) mechanism to the total cross-section for ($\alpha$, $pn$) + ($\alpha$, $d$) was seen to increase with the atomic number, $Z$; however, this was due more to a decrease in the ($\alpha$, $pn$) cross-section than an increase in the ($\alpha$, $d$) cross-section. For $^{238}$U, approximately a third of the total cross section was due to the ($\alpha$, $d$) mechanism.

In this investigation, the $\alpha$-particle bombardment of $^{252}$Cf to form the isomeric states of $^{254}$Es has been performed in an attempt to study the effect of angular momentum on the reaction mechanism.

## EXPERIMENTAL PROCEDURE

The californium target was prepared by electrodeposition as the hydrous oxide. A total of $1{\cdot}62 \times 10^{-2}$ $\mu$g of californium (42% $^{252}$Cf) was plated in an area of 0·05 cm$^2$ on 0·002 in thick gold foil. The target was bombarded in the deflector-channel probe assembly of the 60 in. Crocker Laboratory cyclotron, using the recoil-catcher technique previously described.[6] Aluminium absorbers were used to reduce the incident $\alpha$-particle energies to the desired values.

After bombardment, the thin gold catcher foil (~5 mg/cm$^2$) was removed, dissolved in *aqua regia*, and the solution passed through a small bed of Dowex-1 anion-exchange resin to remove the gold and

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(1) E. SEGRE and A. C. HELMHOLZ, *Rev. Mod. Phys.* **21**, 271 (1949).
(2) J. W. MEADOWS, R. M. DIAMOND and R. A. SHARP, *Phys. Rev.* **102**, 190 (1956).
(3) B. LINDER and R. JAMES, *Phys. Rev.* **114**, 325 (1959).
(4) J. R. HUIZENGA and R. VANDENBOSCH, *Phys. Rev.* **120**, 1305, 1313 (1960).
(5) R. SILVA, Report UCRL-8678 (1959).
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some fission products. Separation into individual actinide-element fractions was achieved by elution from Dowex-50 cation-exchange resin with a solution of ammonium α-hydroxy*iso*butyrate.[7] The einsteinium fraction was electrodeposited on a platinum counting disc. $^{241}$Am was used as a chemical yield tracer in these separation steps.

The amount of $^{254m}$Es[$t_{\frac{1}{2}}(\beta^-) = 37$ hr] was determined by allowing the $^{254}$Fm daughter to achieve secular equilibrium and then counting the sample for 7·2 MeV α-particles of $^{254}$Fm in an ionization grid chamber connected to an α pulse-height analyser. The alpha decay of $^{254g}$Es[$t_{\frac{1}{2}}(\alpha) = 480$ days] could not be measured at that time, as the $^{253}$Es formed in the bombardment prevented observation of its decay. After an interval of 10–12 months, the samples were recounted for the $^{254g}$Es radiations.

## RESULTS

Bombardments were performed at the following energies (with total beam in parentheses): 27·9 MeV (5·5 μA hr), 30·0 MeV (14·9 μA hr), 33·6 MeV (3·34 μA hr), 36·8 MeV (5·6 μA hr). Five bombardments with a total beam of 48·9 μA hr were done at 40·0 MeV. Cross-sections calculated for the amount of $^{254m}$Es observed at each energy agreed closely with the excitation function reported earlier.[8] Within the counting statistics, no disintegrations of the 6·64 MeV α-particles of the $^{254g}$Es isomer were observed. From the counting time, it was possible to set an upper limit of $1 \times 10^{-3}$ counts/min for $^{254}$Es in each sample. Lower limits for the isomer cross-section ratios could be calculated for each bombarding energy; however, these ratios are quite dependent on the cross-section for $^{254m}$Es and the total beam, so that they are not realistic limits. At 40 MeV, both cross-section and beam were large and a lower limit of thirty-four was calculated for the ratio (i.e., $\sigma_m/\sigma_g \geqslant 34$).

## DISCUSSION

The cross-sections for the formation of the long-lived isomer of $^{211}$Po,[9] $^{234}$Pa[10] and $^{240}$Np[11] by the (α, *pn*) reaction have been reported. SILVA has measured the total cross-section for the (α, *pn*) reaction for $^{209}$Bi and $^{238}$U by a scattering-chamber method.[8] For (α, *pn*) reactions with other nuclei, his cross-sections are in acceptable agreement with values reported from radiochemical techniques. Since the trends in the isomer cross-section ratios are the subject of this discussion, and not the absolute values, it is possible to use SILVA's data to estimate these ratios. Although the total cross section for the formation of $^{234}$Pa has not been reported, the measured value for that of the long-lived state is so large that the cross-section for the short-lived state cannot be more than 10 mbarns and is probably closer to 5 mbarns. The spins listed for the isomeric states are "best guess" values based on the present evidence.[13] All cross sections given in Table 1 were measured at an α-bombarding energy of 40 MeV; the values in parentheses are estimated from SILVA.

To understand the pattern in the isomer cross-section ratios of Table 1, it is useful to calculate the relative density $P_j/P_0$ of states of spin $J$ by the equation:[14]

$$P_j/P_0 = (2J + 1) \exp\left[-(J + \tfrac{1}{2})^2/2\sigma^2\right].$$

When a value of $\sigma = 4$, based on reported values for $\sigma$ over a wide range of mass

[7] G. R. CHOPPIN, B. G. HARVEY and S. G. THOMPSON, *J. Inorg. Nucl. Chem.* **2**, 66 (1956).
[8] T. SIKKELAND, S. AMIEL and S. G. THOMPSON, *J. Inorg. Nucl. Chem.* **11**, 261 (1959).
[9] F. N. SPIESS, *Phys. Rev.* **94**, 1292 (1954).
[10] B. M. FOREMAN, W. M. GIBSON, JR., R. A. GLASS and G. T. SEABORG, *Phys. Rev.* **116**, 382 (1959).
[11] R. VANDENBOSCH, T. D. THOMAS, S. E. VANDENBOSCH, R. A. GLASS and G. T. SEABORG, *Phys. Rev.* **111**, 1358 (1958).
[12] W. JENTSCHKE, A. C. JUVELAND and G. H. KINSEY, *Phys. Rev.* **96**, 231 (1954).
[13] F. ASARO (Lawrence Radiation Laboratory). Private communication (1960).
[14] C. BLOCH, *Phys. Rev.* **93**, 1094 (1954).

numbers,[4,15] is used, it is possible to calculate that the level density passes through a maximum between $J = 3$ and $J = 4$ (Fig. 1). According to SILVA, the probable mechanism for the reactions yielding ($\alpha$, $pn$) products is emission of high-energy deuterons and protons by direct-interaction processes. When a proton is emitted,

TABLE 1

| Reaction | Total cross-section (mbarns) | Product spins | Isomer cross-section (mbarns) | Estimated ratio $\frac{\text{low spin}}{\text{high spin}}$ |
|---|---|---|---|---|
| $^{209}$Bi($\alpha$, $pn$)$^{211}$Po | $18 \pm 3$ | $\frac{9}{2}^{(12)}$<br>$\frac{1}{2}^{9} - \frac{2}{2}^{5}$ | ($\sim$15)<br>1·5 | $\sim$10 |
| $^{232}$Th($\alpha$, $pn$)$^{234}$Pa | — | 0, 1<br>3, 4 | ($\sim$5–10)<br>21 | $\geqslant$0·5 |
| $^{238}$U($\alpha$, $pn$)$^{240}$Np | 9·6 $\pm$ 1·9 | 1<br>5 | ($\sim$3)<br>6 | $\sim$0·5 |
| $^{252}$Cf($\alpha$, $pn$)$^{254}$Es | — | 2<br>7 | 6<br>$\leqslant$0·2 | $\geqslant$34 |

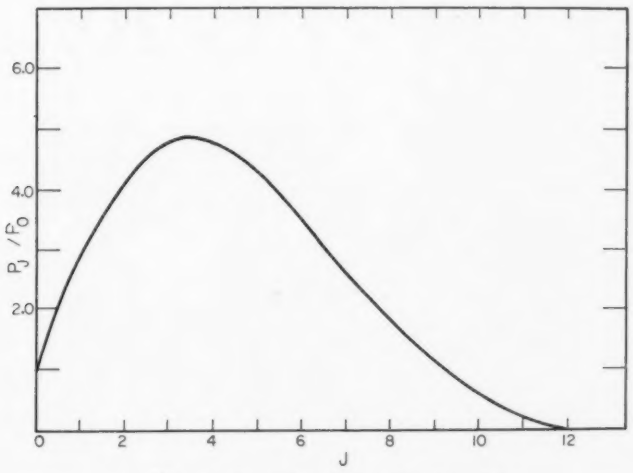


FIG. 1.—Level density as a function of $J$.

evaporation of a neutron follows. In either case, ($\alpha$, $d$) or ($\alpha$, $pn$), there is little angular momentum transfer—perhaps 1 or 2 units. The residual nucleus after completion of the direct processes would be expected to have spins of approximately two for $^{232}$Th and $^{238}$U. This is intermediate between the spins of the isomeric states in both cases and, since the level density for state of $J = 3$, 4, or 5 is greater than for those of $J = 0$ or 1, there will be greater relative population of these states upon deexcitation by neutron evaporation or $\gamma$-emission. This in turn leads to greater population of the

[15] A. C. DOUGLAS and N. MACDONALD, *Nucl. Phys.* **13**, 382 (1959).

higher spin state than of the lower spin state. In fact, this analysis favours a higher ratio in the isomer cross-sections for $^{240}$Np than $^{234}$Pa, and the ratio does seem to be higher.

The spin of $^{209}$Bi is $\frac{9}{2}$, so the excited residual nuclei could have spins ranging from $\frac{5}{2}$ to $\frac{13}{2}$. Since both spin and level density favour the low spin isomer in this case, as expected, the ratio is large. The same situation is true for $^{254}$Es. Even though the differences in level densities for states of $J = 2$ and $J = 7$ in $^{254}$Es are less than for states of $J = \frac{9}{2}$ and $J = \frac{19}{2}$ in $^{211}$Po, the isomer cross-section ratio is larger for $^{254}$Es. This indicates that the value of the spin of the excited nucleus must be very close to that of the metastable state ($I = 2$), so that the latter is greatly favoured in the $\gamma$-cascade.

SILVA's data indicate that for heavy elements the ($\alpha$, $pn$) reaction cross section decreases as $Z$ increases, while the ($\alpha$, $d$) reaction cross section remains relatively constant with $Z$. These trends indicate that for $^{238}$U, $\sigma_{\alpha,pn}/\sigma_{\alpha,d} \sim 2$, while for $^{252}$Cf, the ($\alpha$, $d$) reaction is the principal contributor to the cross-section.

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# CHEMICAL EFFECTS OF $\beta$-DECAY FROM $^{132}$Te TO $^{132}$I*

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**Abstract**—The chemical form of daughter iodine activity produced by $\beta$-decay of $^{132}$Te in the presence of iodine carriers has been investigated. Three forms of iodine can be distinguished: periodate, iodate and reduced forms. The distribution among these forms has been found to be partly dependent on the nature of substances present during growth and also on the oxidation state of the tellurium parent.

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THE $\beta$-decay chain: 77 hr $^{132}$Te · · · 2·4 hr $^{132}$I offers excellent chemical circumstances for study of the consequences of $\beta$-decay. The two half-lives are of convenient magnitudes; there are three distinguishable forms available to the daughter iodine activity; $IO_4^-$, $IO_3^-$, and reduced forms ($IO^-$, $I_2$, $I^-$); the tellurium parent may be present in either of two oxidation states, Te(IV) or Te(VI). An earlier investigation[1] indicated that the iodine appears chiefly in reduced forms, but no systematic investigation of the effect of various growth conditions was reported.

The physical processes which influence the chemical fate of the daughter atom in $\beta$-decay have been fully discussed by EDWARDS and DAVIES.[2] In addition to the immediate increase of one unit on the oxidation number, the daughter atom will be activated by two other effects: recoil from the departing electron and neutrino, and electronic excitation through interaction of the nuclear process with the extra-nuclear electronic structure. Either of these may provide the energy necessary to break bonds or initiate reaction with the substrate. In the present case the decay mechanism of 77 hr Te includes several prompt gammas, one of which may be highly internally converted[3] thus leading to the additional possibility of chemical effects of the same origin as those observed in internally converted isomeric transitions.[4] It is impossible to assess the relative significance of these effects *a priori* but in any event the product-determining events in the case of iodine formed by $\beta$-decay might be similar to those in the case of iodine formed by the $(n,\gamma)$ reaction. If this is the case one may expect that the product distribution in $\beta$-decay may bear some resemblance to that observed in the $(n,\gamma)$ reaction and previously reported from these laboratories.[5]

## EXPERIMENTAL

The 77 hr Te activity used in these experiments was separated from mixed uranium fission products and furnished to us by the Hot Laboratory of the Brookhaven National Laboratory of Upton, Long

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[1] T. H. DAVIES, *J. Phys. Colliod Chem.* **52, 595** (1948).
[2] R. R. EDWARDS and T. H. DAVIES, *Nucleonics* **2**, No. 6, 44 (1948).
[3] T. B. NOVEY, W. H. SULLIVAN, C. D. CORYELL, A. S. NEWTON, N. R. SLEIGHT and O. JOHNSON, *Radio Chemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN), NNES, Plutonium Project Record Div. IV, Vol. 9, Paper 135. McGraw-Hill, New York (1951).
[4] R. R. WILLIAMS, *J. Chem. Phys.* **16**, 513 (1948).
[5] R. E. CLEARY, W. H. HAMILL and R. R. WILLIAMS, JR., *J. Amer. Chem. Soc.* **74**, 4675 (1952).

Island, N.Y. The activity was received as a basic solution of tellurium dioxide containing about one millicurie of activity per milligram of Te. Studies of the decay of Te(IV) were made with diluted samples of this solution to which various reagents were added. Activity in the Te(VI) form was prepared by addition of carrier Te(IV) to the active solution followed by precipitation of silver tellurite and by oxidation of the latter with bromine, yielding a telluric acid solution.[6]

It was found that in order to obtain complete and reproducible recovery of daughter iodine activity it is necessary to have carriers for all three fractions of iodine activity present during the growth period. Accordingly, solutions for study of the decay in acid media contained $2{\cdot}4 \times 10^{-3}$ M $I_2$, $8 \times 10^{-3}$ M iodic acid and $3{\cdot}5 \times 10^{-6}$ M sodium periodate. Periodate must be kept below $10^{-4}$ M; otherwise it oxidizes Te(IV).

The active solution of Te(IV) or Te(VI) in small volume was added to the solution of iodine carriers which had been previously chilled in ice-water. The solutions were then allowed to stand in ice water for radioactive growth for at least 16 hr so that a completely new "generation" of daughter activity was formed under controlled conditions. The reduced temperature was required in order to minimize reaction among the carriers and the oxidation of Te(IV) in basic solutions. Independent tests showed that such oxidation occurred to an extent of 10 per cent or less during the growth period.

After the growth period additional iodate and periodate carriers were added in amount sufficient to make the ultimate silver iodide precipitates weigh approximately 35 mg. This aqueous solution was next shaken with an equal volume of carbon tetrachloride containing dissolved iodine in amount sufficient to make the ultimate reduced fraction silver iodide precipitate weigh approximately 35 mg. The aqueous layer was separated and shaken with a second portion of carbon tetrachloride which was added to the first to constitute the reduced states fraction of the iodine activity.

The next step was to remove parent tellurium activity from the aqueous solution. This was accomplished by addition of carrier Te(IV) and adjustment of the pH to a value of three. The resulting $TeO_2$ precipitate was removed by centrifugation and discarded. (In the study of Te(VI) decay the method of preparation introduced Te(VI) carrier, but the foregoing parent removal step was not carried out, since no insoluble oxide or hydroxide of Te(VI) forms.)

The aqueous solution containing iodate and periodate activity and carriers was treated as follows: An aliquot of the solution was reduced to iodine by hydroxylamine hydrochloride and extracted into carbon tetrachloride. This constituted the total oxidized states fraction of the iodine activity.

A second aliquot of the solution was added to a twenty-five-fold excess of barium chloride in aqueous solution. The resulting precipitate, $Ba(IO_3)_2{\cdot}H_2O$, was filtered, washed and dissolved in nitric acid. This solution was reduced with hydroxylamine hydrochloride and the resulting iodine extracted into carbon tetrachloride to constitute the iodate fraction of the iodine activity.

All three fractions, each consisting of iodine in carbon tetrachloride, were extracted into aqueous metabisulphite solution, acidified and precipitated as silver iodide. The precipitates were washed, dried at 110°, cooled and counted with a common end-window Geiger tube in a lead shield.

A minor contamination of the original material by 8 day $^{132}I$ was present and this was either eliminated from consideration by counting through 278 mg Al/cm$^2$ or corrected for by subtracting the count rate after 24 hr, when all 2·4 hr iodine had decayed. All count-rates were corrected to time of separation.

Experiments in basic media were performed with a somewhat different combination of iodine carriers, namely, $7{\cdot}4 \times 10^{-5}$ M iodide, $7{\cdot}4 \times 10^{-4}$ M iodate and $4 \times 10^{-5}$ M periodate. At the conclusion of growth iodate and periodate were added as before, amounting to $10^{-2}$ M. Then the solution was rapidly acidified, causing the formation of iodine through reaction of iodide and iodate. However, the total oxidation of the iodide consumes less than one per cent of the iodate. From this point separation of the three fractions of iodine activity proceeded as before.

## RESULTS AND DISCUSSION

In several experiments the total activity collected in the three fractions was compared with total iodine activity as determined by the method of GLENDENIN and METCALF.[7] In view of the difficulties encountered in obtaining complete recovery

[6] G. T. SEABORG, G. FRIELANDER and J. W. KENNEDY, *J. Amer. Chem. Soc.* **62**, 1309 (1940).
[7] L. E. GLENDENIN and R. P. METCALF, *Radio Chemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Div. IV, Vol. 9, Paper 278, McGraw-Hill, New York (1951).

of iodine from fission product mixtures it was not surprising to find in these experiments that complete recovery of iodine was not obtained unless all three forms of iodine carrier were present during growth. In all results reported below this condition was fulfilled as described in the preceding section.

It was found that the presence of mild oxidizing or reducing agents present during the growth period altered the distribution of activity in the expected manner, although not to a large degree. Data showing the effect of various concentrations of nitrate ion are given in Table 1 and it is clear that a limiting effect is obtained at a concentration of 1 M. That is, it appears that the oxidizing agent has, at this concentration, exerted its full effect. Similar limiting effects for other oxidizing and reducing agents were observed and in all following cases only the limiting effect is reported.

TABLE 1.—EFFECT OF $NO_3^-$ ON ACTIVITY DISTRIBUTION DECAY OF Te(IV) AT pH = 2·5

| $NO_3^-$ (M/l.) | Activity distribution | |
|---|---|---|
| | Reduced state (%) | Oxidized states (%) |
| 0 | 77 | 23 |
| 0·01 | 77 | 23 |
| 0·1 | 75 | 25 |
| 1·0 | 70 | 30 |
| 2·0 | 70 | 30 |

Tables 2 and 3 summarize the results of analysis of the iodine activity distribution under a variety of conditions. The reliability of the determinations is estimated to be $\pm 2$ per cent.

The result obtained from decay of Te(IV) in acid solution with extra periodate carrier (item 5 in Table 2) requires particular comment. As noted in the preceding sections, periodate shows a tendency to oxidize Te(IV) in acid solutions. While the amount of oxidation is negligible with the usual carrier mixture, in which the concentration of periodate was $3{\cdot}5 \times 10^{-6}$ M, in those systems marked "extra $IO_4^-$", the concentration was increased to as much as 4 M. This is more than sufficient to oxidize the Te(IV) to Te(VI) in short a time in acid solution and the result in item 5 of Table 2 almost certainly applies to Te(VI). It is, in fact, experimentally indistinguishable from item 4 in Table 3.

The data in Tables 2 and 3 show a variation in the distribution of iodine activity depending on the presence or absence of oxidizing or reducing agents. This variable fraction shifts between iodate and the reduced states and amounts to *ca.* 13 per cent in acid solutions and *ca.* 22 per cent in basic solutions. A similar but greater variability in distribution was noted in the $(n,\gamma)$ reaction and was assigned to a hypothetical unstable $IO_2^-$ intermediate. The same hypothesis is tenable in this case since it appears that the variable fraction shifts chiefly between iodate and reduced forms rather than appearing in periodate.

After correcting for the variable fraction, the irreducible yield of the product expected if no bonds are broken (iodate from tellurite and periodate from tellurate) is rather small, 10 per cent or less. This indicates that the $\beta$-decay process must strongly

TABLE 2.—IODINE ACTIVITY DISTRIBUTION FROM DECAY OF Te(IV)

| pH | Additives | Activity distribution (%) | | |
|---|---|---|---|---|
| | | Reduced states | Iodate | Periodate |
| 2·5 | Carriers only | 77 ± 2 | 16 ± 2 | 7 ± 2 |
| 2·5 | $CH_3OH$ | 84 | 10 | 6 |
| 2·5 | $NO_3^-$ | 71 | 22 | 7 |
| 2·5 | $ClO_4^-$ | 72 | 21 | 7 |
| 2·5 | Extra $IO_4^-$ (see text) | 70 | 16 | 14 |
| 13·5 | Carriers only | 66 | 26 | 8 |
| 13·5 | $CH_3OH$ | 84 | 10 | 6 |
| 13·5 | $NO_3^-$ | 62 | 28 | 10 |
| 13·5 | Extra $IO_4^-$ (see text) | 62 | 25 | 13 |

TABLE 3.—IODINE ACTIVITY DISTRIBUTION FROM DECAY OF Te(VI)

| pH | Additives | Activity distribution (%) | | |
|---|---|---|---|---|
| | | Reduced states | Iodate | Periodate |
| 2·5 | Carriers only | 72 ± 2 | 14 ± 2 | 14 ± 2 |
| 2·5 | $CH_3OH$ | 81 | 7 | 12 |
| 2·5 | $NO_3^-$ | 67 | 19 | 14 |
| 2·5 | Extra $IO_4^-$ (see text) | 68 | 16 | 16 |
| 13·5 | Carrier only | 58 | 24 | 18 |
| 13·5 | $CH_3OH$ | 76 | 10 | 14 |
| 13·5 | $NO_3^-$ | 54 | 28 | 18 |

TABLE 4.—DISTRIBUTION OF ACTIVITY FROM GROWTH IN SOLID $TeO_2$

| Dissolving reagent | Activity distribution (%) | | | |
|---|---|---|---|---|
| | Reduced | Iodate | Periodate | Total |
| 4 N NaOH | 52 | 8 | 6 | 66 |
| plus iodine carriers | 41 | 54 | 5 | 100 |

activate the ion in which the decay occurs. In fact, the activation would appear to be greater in $\beta$-decay than in neutron capture, since (a) the yield of reduced states is greater from tellurate $\beta$-decay than from neutron capture by periodate and (b) periodate is formed in $\beta$-decay from tellurite, whereas it is not formed in neutron capture by iodate. However, the oxidation to periodate and indeed a substantial part of the total reaction observed could be attributed to the internal conversion process reported in the decay scheme.[3,4]

The methods developed for analysis of iodine daughter activity were also applied

to the product obtained from the "milking" procedure developed at the Brookhaven Hot Laboratory.[8] In this procedure the iodine daughter activity is grown in a moist $TeO_2$ precipitate containing several millicuries of $^{132}$Te. The precipitate is dissolved in 4 N sodium hydroxide solution. $TeO_2$ is then reprecipitated by addition of formic acid and the filtrate, containing the iodine activity, is removed. We have determined the yield and distribution of this activity under several conditions as shown in Table 4. It is clear that growth in solid $TeO_2$ yields a large fraction of iodate activity, but that extraction without carriers (which is the usual procedure) does not recover this fraction, but only the reduced fraction.

[8] L. G. Stang, Jr., W. D. Tucker, H. O. Banks, Jr., R. F. Doering and T. H. Mills, *Nucleonics* **12**, No. 8, 22 (1954).

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# THE REACTIONS OF RECOIL TRITIUM ATOMS IN AQUEOUS SOLUTION†

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**Abstract**—Tritium atoms recoiling from $Li^6(n,\alpha)H^3$ in approximately 1 M LiCl or $LiNO_3$ aqueous solution form HT and HTO in the ratio of 0·10 ± 0·01 under most conditions. In 15·9 M $Ca(NO_3)_2$ solutions, the HT/HTO ratio decreases only to 0·023. An important reaction leading to HT formation is the hot abstraction reaction $T^* + H_2O \rightarrow HT + OH$.

TRITIUM atoms recoiling from the nuclear reactions $Li^6(n,\alpha)T$ or $He^3(n,p)T$ have been shown to react chemically with many organic molecules, while still possessing some of the kinetic energy from nuclear recoil.[1] In contrast to the study of organic species, few studies of reactions with inorganic molecules have been reported. The distribution of recoil tritium between HT and HTO was first measured for tritium atoms formed in the spallation of oxygen by 2·2 BeV protons.[2] The HT/HTO ratio, in a target solution of 0·1 N $HNO_3$, was determined as 0·11. Recoil tritium atoms formed in some aqueous solutions have been reported to give large amounts of labile tritium, with small percentages of molecular HT also being observed.[3,4]

Two simple reactions for a tritium atom and a single water molecule are the hydrogen abstraction reaction:

$$T + HOH \rightarrow HT + OH \qquad (1)$$

and the isotopic exchange reaction:

$$T + HOH \rightarrow TOH + H \qquad (2)$$

In the gas phase, reaction (1) is endothermic by about 14 kcal/mole, which leads to an activation energy of 23–24 kcal/mole when combined with the activation energy of 9–10 kcal/mole observed for the reverse reaction.[5] This reaction is not observed

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[1] Recent summaries of these reactions have appeared in *Canad. J. Chem.*, **38,** 1756 (1960), (Authors: J. K. LEE, BURDON B. MUSGRAVE and F. S. ROWLAND); and in the papers prepared for the forthcoming volume on the Symposium on the Chemical Effects of Nuclear Transformations, sponsored by the I.A.E.A. and held in Prague, Oct., 1960. (F. S. ROWLAND, J. K. LEE, B. MUSGRAVE and R. M. WHITE; *The Reactions of High Kinetic Energy Tritium Atoms from Nuclear Recoil*).

[2] E. L. FIREMAN and F. S. ROWLAND, *Phys. Rev.* **97,** 780 (1955).

[3] H. KELLER and F. S. ROWLAND, *J. Phys. Chem.* **62,** 1373 (1958).

[4] L. KAPLAN and R. WOLFGANG. Private communication.

[5] Energies estimated from the values for protium given in S. BENSON, *The Foundations of Chemical Kinetics* p. 454. McGraw-Hill (1960) page 454, ignoring isotopic differences. BENSON quotes 9 ± 3 kcal/mole for the activation energy of the reverse reaction to (1), from the data of R. R. BALDWIN, *Trans. Faraday Soc.* **52,** 1337, 1344 (1956). A value of 10 kcal/mole is quoted by N. N. SEMENOV, *Some Problems in Chemical Kinetics and Reactivity*, translation by M. BOUDART, Princeton Volume 1, p. 149, University Press, (1958) from the data of L. I. AVRAMENKO, *Acta Physicochem.* URSS, 197 (1942), for the same reverse reaction.

in the reactions of thermal hydrogen atoms (25°C) in the gas phase with water-vapour,[6] and is uniformly assumed not to occur in the liquid phase for the hydrogen atoms formed in the radiolysis of water.[7] Reaction (2) has been estimated variously to have an activation energy in the gas phase of 18 kcal/mole[6] and 12 kcal/mole.[8] The reverse of reaction (1) occurs readily in aqueous solutions under irradiation.

Tritium atoms may also react readily in the liquid phase by radical recombination reactions with H atoms and CH radicals to form HT and HTO reactions (3) and (4), for which the activation energies should be approximately zero.

$$T + H \rightarrow HT \tag{3}$$

$$T + CH \rightarrow TOH \tag{4}$$

We have irradiated aqueous solutions of lithium salts between pH 1 and 14, in both air-saturated and air-free solutions, and in the presence of other salts, in order to determine the relative contributions of reactions (1)–(4), and other possible reactions to the observed yields of HT and HTO.

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## EXPERIMENTAL

*Chemicals.* Reagent grade chemicals were generally used without further purification. $CO_2$-free water was prepared for the solutions of pH greater than 9; ordinary distilled water was used for other solutions. All solutions contained 0·7 M to 1·5 M $Li^+$ ions in the normal isotopic abundance as targets for the $Li^6(n,\alpha)T$ reaction. Other solutes were added to adjust the pH value, or to introduce other ions into the solution.

*Preparation of samples for irradiation.* Samples of about 1·5 ml were sealed in 1720 Pyrex glass tubes (D.C. 10 mm) which had volumes of 4–5 ml and were equipped with break-tips. Most of the samples were sealed in the absence of air after distillation *in vacuo*; some were sealed with air present either at 1 atm or at reduced pressures.

*Irradiations.* The irradiations were carried out either at the Argonne or Brookhaven National Laboratories for a total flux of $10^{14}$–$10^{15}$ neutrons/cm$^2$. The actual flux inside the tubes was reduced from the nominal fluxes in the irradiation facilities by neutron absorption in the 1720 Pyrex and by self-shielding in large groups of samples. Series B, C, and D received $2 \times 10^9$ neutrons cm$^{-2}$ sec$^{-1}$ for six days; A and E received $1 \times 10^{12}$ neutrons cm$^{-2}$ sec$^{-1}$ for 30 min; F, G, and H received $2 \times 10^{12}$ neutrons cm$^{-2}$ sec$^{-1}$ for 15 minutes.

*Measurement of HT activity.* After irradiation, the sample tubes were opened in a vacuum line in the presence of $H_2$ (occasionally $^4He$) serving as a carrier gas for the HT formed during the irradiation, and the mixed sample and carrier gases were alternately heated and frozen two or three times with liquid nitrogen to insure good mixing. The non-condensable gases were then expanded into a silver-walled, gas proportional counter of 100 cm$^3$ volume, 85 cm$^3$ active counting volume, while the side arm and irradiated solution were immersed in a liquid nitrogen bath to a carefully controlled depth. A good counter filling was obtained by adding 40 cm Hg of propane gas to the counter, and the HT activity was measured.

A second aliquot of the HT gas was also taken as a check on the reliability of the assay—the ratio of activities of successive aliquots served as a measure of the fractional distribution of gaseous radioactivity between the counter and the remainder of the system under the experimental conditions of extreme temperature gradients. Separate calibration experiments showed that no HTO activity entered the counter under these experimental conditions.

*Measurement of HTO activity.* Two or more aliquots of the aqueous solutions were determined by sealing about 10 mg into a weighed capillary, conversion of HT by the zinc combustion method, and assay with the same proportional counter procedure.* The small amounts of air present in some

* The general counting procedures involved in our laboratory have been described in ROWLAND, *et al.*[9]

[6] R. F. FIRESTONE, *J. Amer. Chem. Soc.* **79**, 5593 (1957), for the corresponding D reaction.
[7] See, for example, F. S. DAINTON, *Radiation Research*, Supplement 1, 1–25 (1959).
[8] P. HARTECK, *J. Chem. Phys.* **22**, 1746 (1954) from the deuterium data of K. H. GEIB and E. W. R. STEACIE, *Z. Phys. Chem.* B **29**, 215 (1935).
[9] F. S. ROWLAND, J. K. LEE and R. M. WHITE, U.S.A.E.C. Report TID–7587, p. 39–48, (1959).

non-condensable aliquots did not interfere with the tritium assay. Separate tests showed that as much as 1 cm Hg of air could be tolerated in the proportional counter under these operating conditions before the counting plateau versus voltage deteriorated sufficiently to make assay difficult.

## RESULTS

The HT/HTO ratios observed from the irradiated solutions are collected in Table 1, together with the composition of each sample. At all pH's from 1 to 11, for both air-saturated and air-free solutions, the ratios fall between 0·09 and 0·12, and have a constant value within the experimental error. The samples at pH 13–14 or with dissolved salts present usually gave HT/HTO values near this ratio, but were definitely different in several cases. In no case did the amount of tritium found as HT exceed 30 per cent of that found as labile tritium in the system.

DISTRIBUTION OF RECOIL TRITIUM BETWEEN HT AND HTO IN AQUEOUS SOLUTIONS

(a) All of the experiments summarized in this part gave an HT/HTO ratio in the range 0·09 to 0·12, with an average value of 0·10 ± 0·01.

| | |
|---|---|
| A-2 | 1·5 M $LiNO_3$ |
| B-1 to B-9 | 1·5 M $LiNO_3$, 0·05 M $SO_4^{2-}$–$H_2SO_4$ or LiOH to adjust pH from 1 to 11; six air-saturated samples, three air-free. |
| C-1 and C-2 | 1·5 M $LiNO_3$, pH 6; one air-saturated, one air-free |
| D-1 to D-9 | 1·6 M $LiNO_3$, $HNO_3$ or LiOH to adjust pH from 1 to 11; six air-saturated samples, three air-free. |
| F-1 to F-4 | 0·7 M LiCl, two air-saturated, two air-free |
| F-6 to F-11 | 0·7 M LiCl, pH 9–13, one with 50 cm Hg $H_2$ gas at pH 13, others air free |
| G-2 | 0·7 M LiCl, 0·1 M NaOH, air free |
| H-1 to H-8 | 0·7 M LiCl, saturated with various solutes (amounts in parentheses per 100 g of water): KCN (80 g); $Na_3PO_4 \cdot 12H_2O$ (11 g); $I_2$ (0·03 g); KI + $I_2$ (0·1 g); $KIO_4$ (0·7 g); $NH_4HCO_3$ (21 g); $NH_4Cl$ (37 g); Benzene (0·07 g).† |

(b)

| | | HT/HTO ratio |
|---|---|---|
| A-1 | 1·5 M $LiNO_3$, 0·1 M NaOH | 0·06 |
| E-1 | 1·5 M $LiNO_3$, 0·1 M NaOH | 0·08 |
| E-2 | 0·6 M LiOH | 0·04 |
| F-5 | 0·7 M LiCl, pH 14 | 0·048 |
| G-1 | 1·0 M LiCl, 1 M NaOH | 0·07 |

(c) H series, all 0·7 M LiCl

| | Saturated with | Approx. solubility (grammes of anhydrous salt) per 100 g of water) | HT/HTO |
|---|---|---|---|
| H-9 | $Na_2Cr_2O_7 \cdot 2H_2O$ | 180 | 0·06 |
| H-10 | $CH_3COONa$ | 125 | 0·30* |
| H-11 | $NaNO_3$, pH = 10 | 90 | $0·03_8$ |
| H-12 | $NaNO_3$, pH = 13 | 90 | $0·03_8$ |
| H-13 | $Ca(NO_3)_2 \cdot 4H_2O$ | 130 | $0·02_4$ |
| H-14 | $Ca(NO_3)_2 \cdot 4H_2O$ 21 cm air | 130 | $0·02_2$ |
| H-15 | 2 parts 0·7 M LiCl 1 part sat. $Ca(NO_3)_2$ solution | | $0·05_3$ |
| H-16 | 1 part 0·7 M LiCl 2 parts sat. $Ca(NO_3)_2$ solution | | $0·03_4$ |

* Ratio of non-condensable (−196°C) activity to condensable activity.

*Radiation doses*

The total radiation dose for a sample is unimportant for these experiments unless the dosage is high enough to cause appreciable radiation alteration of the primary products. Our experimental conditions, including the nature of the radiations and the free volumes of the irradiation tubes, are comparable to the experiments of SOWDEN, in which the yield of hydrogen gas was shown to be linear with dose to $7 \times 10^{22}$ eV/g of solution for $Ca(NO_3)_2$ solutions in the concentration ranges from 15·9 to 0·037M.[10] The radiation damage to our solutions is caused both by the alphas and tritons from the $^6Li(n,\alpha)T$ reaction and by the $\gamma$-ray background of the reactor. The energy deposited ranged from $10^{19}$ to $10^{20}$ eV/g of solution, and is thus well within the linear hydrogen range. An experiment with 0·7 M LiCl solution saturated with $KMnO_4$ showed an HT yield of zero, consistent with the recent observations of DANIELS on the rapid radiation-induced removal of $H_2$ from permanganate solution.[11] With this exception, and at pH 13–14, the removal of HT by subsequent radiation effects should not be significant here.

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## DISCUSSION

*Hot vs. thermal reaction*

Since qualitative identification of labeled HT and HTO is consistent with both the thermal atom recombinations (3) and (4) and the hot atom reactions (1) and (2), our primary concern is to distinguish between these possibilities. The hot reactions, by analogy with similar reactions for organic molecules,[12] are expected to occur with all species present in rough proportion to the amount of each present, and therefore to form HT and HTO in the same proportion in all dilute solutions, and in similar proportions in concentrated solutions.

None of these reactions has, of course, been carried out in pure water, or even in very dilute aqueous solution, since each sample was at least 0·7 M in $Li^+$ ion plus the corresponding negative ion. The hydrogen atom recombination reaction, however, is sensitive to the presence of certain hydrogen atom scavengers, such as $O_2$, $NO_3^-$, etc.,[13,10] which bind the H atom to oxygen ($HO_2$, $OH^-$) with a resultant decrease in $H_2$ formation. Similarly, the OH radical reactions are altered by reaction with other scavengers, including $Cl^-$, $Br^-$, which form $OH^-$.[13]

The most pertinent experiments bearing on the question of hot versus thermal atom reaction are those performed with saturated solution of $Ca(NO_3)_2$. The $NO_3^-$ ion has been shown to be an excellent scavenger for thermal hydrogen atoms, and is believed to remove it by reaction (5).[10]

$$H + NO_3^- \rightarrow NO_2 + OH^- \qquad (5)$$

Nevertheless the observed percentage yield of HT from tritium recoil in saturated calcium nitrate solution is reduced only by a factor of four from that obtained in 0·7 M $Cl^-$ solutions containing no nitrate ion at all.

In contrast, nitrate scavenging of thermal hydrogen atoms competes so successfully with hydrogen atom recombination that mixed fast neutron plus $\gamma$-irradiated 15·9 M $Ca(NO_3)$ solutions show a seventy-fivefold reduction in $G(H_2)$ from the value

[10] R. G. SOWDEN, *Trans. Faraday Soc.* **55**, 2084 (1959).
[11] M. DANIELS, *J. Phys. Chem.* **64**, 1839 (1960).
[12] J. K. LEE, B. MUSGRAVE and F. S. ROWLAND, *J. Amer. Chem. Soc.* **82**, 3545 (1960).
[13] See for example H. A. SCHWARZ, *J. Amer. Chem. Soc.* **77**, 4960 (1955).

observed for water (0·019 M KBr solution).[14] In the much more densely ionized track left by a recoiling fission product, the 15·9 M nitrate solutions show an eightfold smaller $G(H_2)$ than 0·037 M nitrate solutions.[10,14]

Since the ionizing power of fission fragments is substantially greater than that of recoiling tritium atoms, and the ionizing power of atoms at energies of 10–1000 eV is less than that for the same species at higher energies,[15,16] the conclusion is readily reached that the H atom density near the end of the recoil tritium path is far less than that found in fission recoil paths. Consequently, the failure of concentrated nitrate ion solutions to reduce the HT yield by more than the observed factor of four indicates that a substantial amount of the HT is formed by non-thermal processes, i.e. by reaction (1). Similarly, although the $G$ values for ferrous oxidation (in solutions of 1 mM $FeSO_4$ and 0·8 N $H_2SO_4$ ($+Li_2SO_4$)) during neutron irradiation are 5·69 and 4·10 for aerated and deaerated solutions respectively,[17] the presence or absence of air, or other free radical scavengers such as $I_2$, has no effect on the observed HT/HTO yields in these experiments.

The importance of reaction (1) in aqueous solution is consistent with the experimental observation that recoil tritium reacts in the gas phase with water vapour to give a measurable yield of HT, even in the presence of radical scavengers.[18] The measured HT/HTO ratios in the gas phase ranged as high as 0·04. This is a lower limit for the hot reaction of T with $H_2O$, for all of the gas phase experiments have included large quantities of inert gases, whose effect should be to transform some of the hot yield of HT to thermal reactions forming HTO. The aqueous solution experiments, taken with the gas phase results, indicate that more than 4 per cent, and probably nearly 10 per cent, of the recoil tritium atoms formed in the solutions react by energetic hydrogen abstraction (1). Some contribution from reaction (3) is presumably present also. The yields of reactions (2) and (4) cannot be readily estimated from these experiments.

*Effects of dissolved substances*

The only compounds to have an appreciable effect on the distribution of tritium between HT and HTO are those which were present in the solution in major amounts: sodium acetate, sodium dichromate, and calcium and sodium nitrates. Each of these solutions contained from 47 to 64 weight per cent of the dissolved salt, and reactions of the hot tritium atom directly with the solute must be important. For example, an appreciable diminution in HT yield could be expected in concentrated nitrate ion solution simply from the increase in the mole fraction of nitrate ions present, since hot reaction with nitrate ion should lead to HTO.

Small variations in the HT/HTO ratio may arise from interference with bona fide thermal reactions by the scavenging of H or T atoms or OH radicals by the dissolved solutes. Variations in this ratio might also arise in very concentrated solutions as the fraction of water molecules adjacent to ions is greatly increased.

[14] R. G. SOWDEN, *J. Amer. Chem. Soc.* **79**, 1263 (1957).
H. A. MAHLMAN and J. W. BOYLE, *J. Chem. Phys.* **27**, 1434 (1957).
[15] H. S. W. MASSEY and E. H. S. BURHOP, *Electronic and Ionic Impact Phenomena*. Oxford University Press (1956).
[16] S. K. ALLISON, *Rev. Mod. Phys.* **30**, 1137 (1958).
[17] R. SCHULER and N. F. BARR, *J. Amer. Chem. Soc.* **78**, 5756 (1956).
[18] F. S. ROWLAND, T. KAMBARA and I. HATHAWAY, *Symposium on the Chemical Effects of Nuclear Transformations*, sponsored by I.A.E.A. in Prague, Oct. (1960).

Using four molecules of water per $Ca(NO_3)_2$ as in the stable crystalline form, less than 40 per cent of the water molecules are actually "free" molecules while the majority are "water of hydration" in the concentrated $Ca(NO_3)_2$ solutions. As practically nothing is known concerning reactions of energetic tritium atoms with nitrate ions, or on the possible effect of ion-dipole binding on the course of these energetic reactions with the water molecule, quantitative estimates of any expected variations in HT/HTO cannot be made yet.

Most of the increase in HT yield with concentrated acetate solutions undoubtedly arises from direct attack by the tritium atom on the methyl group of the acetate ion. More than 30 per cent of the hydrogen atoms in this system are bonded to methyl carbons, and hydrogen abstraction by energetic tritium atoms is usually a predominant mode of reaction at saturated carbon atoms. The distribution of tritium activity between condensable and non-condensable molecules in this system is consistent with the most important reactions being "hot" reactions with the water and the acetate ion crudely in proportion to their mole fractions.

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*Effect of pH*

No effect of hydrogen ion concentration is observed in the HT/HTO ratio in the pH range 1–12. At pH 13 and 14, the amount of HT formed is somewhat variable and declines by as much as a factor of two. Strongly basic aqueous solutions, however, show some differences in radiolysis mechanism, involving $O^-$ and chain exchange reactions,[19] and the observed amount of HT may very well be affected by chain-promoted exchange between molecular hydrogen and the labile forms. Since the specific radioactivity of the molecular hydrogen is much greater than that of the labile forms, a reduction in HT yield would be observed under these circumstances.

[19] S. Gordon and E. J. Hart, *J. Amer. Chem. Soc.* **77**, 3981 (1955).

J. Inorg. Nucl. Chem., 1961, Vol. 21, pp. 216 to 220. Pergamon Press Ltd. Printed in Northern Ireland

# LATTICE ENERGIES AND ASSOCIATED THERMODYNAMIC PROPERTIES OF SOME CRYSTALLINE SULPHATES AND OF SILVER SELENATE

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**Abstract**—The lattice energies of some sulphates of univalent and bivalent cations are calculated, and the enthalpy of formation of the gaseous sulphate ion is evaluated. The lattice energy of silver selenate and the enthalpy of formation of the gaseous selenate ion are also calculated.

The solubilities of the sulphates are discussed in terms of the standard free energy of solution and its thermodynamic components.

THE complete evaluation of the lattice energy of a crystalline sulphate has not previously been reported. An approximate calculation of the Madelung constants for calcium, strontium, barium and lead sulphates has been made, assuming them to be of the "sodium chloride" structure type and using as interionic distance the geometric mean of the unit cell dimensions.[1,2] From the values so obtained the following electrostatic components of lattice energy, $U_c$, were listed.

| | $CaSO_4$ | $SrSO_4$ | $BaSO_4$ | $PbSO_4$ | |
|---|---|---|---|---|---|
| $U_c$ | −667 | −648 | −624 | −642 | kcal/mole. |

The true lattice energies must, in fact, be less negative than these values, since no repulsion term has been included in their evaluation. In order to improve these calculations, more accurate Madelung constants are required, together with assumptions regarding the repulsion potentials. The structures of calcium, strontium, barium and lead sulphates are fairly simple, and with the exception of lead sulphate are predominantly ionic. The appropriate Madelung constants were deduced indirectly by the following procedure.

We note first that the low temperature forms of potassium and ammonium borofluorides are isostructural with strontium, barium and lead sulphates; also potassium and ammonium borofluorides exist in high temperature cubic forms, above 300°C, in which the ions are distributed as in the "sodium chloride" lattice type.[3] Thus, their lattice energies, in these forms, may be evaluated from the equation:

$$U'(r_0) = -N/J \,.\, \frac{A(ze)^2}{r_0} \,.\, (1 - \rho/r_0) \qquad (1)$$

[1] Y. SAKAMOTO, *J. Sci. Hiroshima Univ.* **A16**, 581 (1953).
[2] Y. SAKAMOTO, *Bull. Chem. Soc. Japan* **26**, 283 (1953).
[3] R. W. G. WYCKOFF, *Crystal Structures*, Vol. 2. Interscience, New York (1960).

where $A$ is the Madelung constant for the "sodium chloride" structure type, $1/\rho$ is the repulsion exponent[4] and $N, J, z, e, r_0$ have their usual significance.

From their small coefficients of thermal expansion it may be inferred that the lattice energies will not change appreciably over the temperature range 20–300°C, and we may say that the lattice energies calculated by equation (1) are applicable also to the low temperature form of these borofluorides.[5] The crystallographic data used in this and subsequent calculations were taken from the compilation of WYCKOFF.[3] From a consideration of the polarizabilities of the borofluoride ion[5,6] and of the bromide ion,[7] it is considered that the compressibilities of potassium and ammonium borofluorides are similar to those of the corresponding bromides. The values of $r_0$ and $\rho$ used, and the lattice energies $U'(r_0)$ calculated are as follows:

| | $r_0$ (Å) | $\rho$ | $-U'(r_0)$ (kcal/mole) |
|---|---|---|---|
| $KBF_4$ | 3·63(0) | 0·36 | 144 |
| $NH_4BF_4$ | 3·77(5) | 0·41 | 137 |

The values of $U'(r_0)$ are uncorrected for van der Waals and zero-point energy terms. ALTSCHULLER[5] has reported for these borofluorides $U'(r_0)$ values of $-144$ and $-136$ kcal/mole respectively, and has calculated the appropriate van der Waals' terms to be $-9$ and $-10$ kcal/mole. These quantities should not, however, be added directly to the remaining terms in evaluating the complete lattice energy, $U(r_0)$,[8] and we have estimated that the increment should be $-3$ kcal/mole for both salts. Including the zero-point energy of $+1$ kcal/mole, we obtain:

$$U(r_0)\ KBF_4 = -146 \text{ kcal/mole}$$

$$U(r_0)\ NH_4BF_4 = -139 \text{ kcal/mole}$$

In calculating the lattice energies, accurate compressibility data are lacking and we are obliged to assume that the repulsion exponent $\rho$ in equation (1) is constant for this series. To determine whether the "sodium chloride" Madelung constant is applicable to the low temperature orthorhombic form of potassium and ammonium borofluoride we calculate from equation (1) the "equivalent" $r_0$ value which would reproduce the complete lattice energy, $U(r_0)$, obtaining $r_0 = 3{\cdot}58(0)$ Å and $3{\cdot}72(1)$ Å respectively. From crystallographic data relating to the orthorhombic forms we note the configuration of $BF_4^-$ ions around a given cation to be a slightly distorted octahedron, from which the weighted $\bar{r}_0$ values are $3{\cdot}58(6)$ Å and $3{\cdot}73(0)$ Å respectively; the good agreement between these and the "equivalent" $r_0$ values justifies the use of the above Madelung constant if the weighting procedure includes the six nearest neighbour distances.

Since the borofluorides in their orthorhombic form are isostructural with strontium, barium and lead sulphates, we may calculate their lattice energies, $U'(r_0)$, as previously defined, from equation (1) where $A$ is the Madelung constant for the "sodium

[4] L. PAULING, *Z. Krist.* **67**, 377 (1928).
[5] A. P. ALTSCHULLER, *J. Amer. Chem. Soc.* **77**, 6187 (1955).
[6] J. R. TESSMAN, A. H. KAHN and W. SHOCKLEY, *Phys. Rev.* **92**, 890 (1953).
[7] M. BORN and W. HEISENBERG, *Z. Phys.* **23**, 388 (1924).
[8] M. BORN and K. HUANG, *Dynamical Theory of Crystal Lattices*. Oxford Univ. Press (1954).

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chloride" arrangement, and with $z = 2$. The weighted mean values of $\bar{r}_0$ and the corresponding lattice energies are:

| | $\bar{r}_0$ (Å) | $-U'(r_0)$ (kcal/mole) |
|---|---|---|
| $SrSO_4$ | 3·50(7) | 596 |
| $BaSO_4$ | 3·62(8) | 576 |
| $PbSO_4$ | 3·54(0) | 590 |
| $CaSO_4$ | 3·37(5) | 619 |

The value for calcium sulphate was obtained similarly from its relationship to $NaBF_4$; the structure of these compounds differs slightly from that of the $BaSO_4$ group.[3]

From the values of $U'(r_0)$, in conjunction with the Born-Haber cycle in the form:

$$U'(r_0) = \Delta H_f - (I + S) - \Delta H_f\,(SO_4^{2-}\text{ gas}) + nRT \qquad (2)$$

we next calculate the composite term $\Delta H_f\,(SO_4^{2-}\text{ gas})$, which includes the electron affinity of the $SO_4$ group. The thermodynamic data used in equation (2) were taken from recent compilations,[9,10,11] the following results were obtained:

| | |
|---|---|
| from $CaSO_4$ | $\Delta H_f\,(SO_4^{2-}\text{ gas}) = -180$ kcal/g ion |
| from $SrSO_4$ | $-173$ kcal/g ion |
| from $BaSO_4$ | $-179$ kcal/g ion |
| from $PbSO_4$ | $(-193)$ kcal/g ion |

Omitting the value derived from lead sulphate, the mean value of $\Delta H_f\,(SO_4^{2-}\text{ gas}) = -177$ kcal/g ion. This omission is not unreasonable, since the $U'(r_0)$ terms do not include the van der Waals energy contribution, and $Pb^{2+}$ has an electronic configuration for which this term is, in general, large (cf. $Ag^+$, $Tl^+$).[12,13]

We next evaluate the lattice energies $U'(r_0)$ for the sulphates of Group IIA and of silver and thallium(I) using equation (2) with $\Delta H_f\,(SO_4^{2-}\text{ gas}) = -177$ kcal/g ion In Table 1 are listed these lattice energies, together with the heats and entropies of solution, the derived free energies of solution and the heat of hydration of the gaseous sulphate ion. The method of evaluation has been described previously.[12,14]

## DISCUSSION

The values of $\Delta G_s$ show a general relationship with the measured solubilities. Since the quantity $\Delta G_s$ refers to the free energy change for the process: solid $\rightleftharpoons$ ions at unit activity, it may be equated to $-RT \ln (a\pm)^2$. For example:

| | $c$ | $f\pm$ | $a\pm$ | $-RT \ln (a\pm)^2$ |
|---|---|---|---|---|
| $SrSO_4$ | $7{\cdot}35 \times 10^{-4}$ | 0·776 | $5{\cdot}7 \times 10^{-4}$ | 8·8 |
| $BaSO_4$ | $3{\cdot}27 \times 10^{-5}$ | 0·948 | $3{\cdot}10 \times 10^{-5}$ | 12·3 |

[9] O. KUBASCHEWSKI and E. LL. EVANS, *Metallurgical Thermochemistry* (3rd Ed.) Pergamon Press, London (1958).
[10] W. FINKELNBURG and W. HUMBACH, Naturwissenchaften **42**, 35 (1955).
[11] D. R. STULL and G. C. SINKE, *Advances in Chemistry* No. 18. Amer. Chem. Soc. (1956).
[12] M. F. C. LADD and W. H. LEE, *Trans. Faraday Soc.* **54**, 34 (1958).
[13] M. F. C. LADD and W. H. LEE *J. Inorg. Nucl. Chem.* **11**, 264 (1959).
[14] M. F. C. LADD and W. H. LEE *J. Inorg. Nucl. Chem.* **14**, 14 (1960).

The sulphates of beryllium, magnesium and calcium form hydrates and the corresponding term derived from solubility data is not in good agreement with $\Delta G_s$; this means, presumably, that the data on solubility do not refer to the anhydrous compounds. For example, the positive $\Delta G_s$ obtained for beryllium sulphate indicates sparing solubility, whereas literature values of $f\pm$ for this salt are quoted up to 4 molal.[15]

The marked difference in solubility between anhydrous beryllium and magnesium

TABLE 1.*—THE FREE ENERGY OF SOLUTION AND ASSOCIATED THERMODYNAMIC PROPERTIES OF SOME SULPHATES

| | $-U'(r_0)$ | $\Delta H_s$ | $\Sigma S_i^0$ | $S_L$ | $T\Delta S_s$ | $\Delta G_s$ | $-\Delta H_h(So_4^{2-}gas)$ |
|---|---|---|---|---|---|---|---|
| $BeSO_4$ | 821 | −19·1 | −50·9 | 21·5 | −21·6 | 2·5 | 224 |
| $MgSO_4$ | 686 | −21·8 | −24·1 | 21·9 | −13·7 | −8·1 | 229 |
| $CaSO_4$ | 621 | −4·3 | −9·1 | 25·5 | −10·3 | 6·0 | 226 |
| $SrSO_4$ | 591 | −2·1 | −5·3 | 29·1 | −10·3 | 8·2 | 228 |
| $BaSO_4$ | 578 | 4·6 | 7·1 | 31·6 | −7·3 | 11·9 | 227 |
| $RaSO_4$ | 562 | 9·1 | 17·1 | 34·0 | −5·0 | 14·1 | — |
| $Ag_2SO_4$ | 478 | 4·5 | 39·4 | 47·8 | −2·5 | 7·0 | 234 |
| $Tl_2SO_4$ | 411 | 7·6 | 64·9 | 52·8 | 3·6 | 4·0 | 239 |

Mean $\Delta H_h(SO_4^{2-}$ gas) = −229 kcal/g ion.

* $H$, $G$ and $T\Delta S$ terms are in kcal/mole entropies, $S$ terms are in cal/mole degree.

sulphates is seen to depend almost entirely on the difference in entropy of the hydrated cations, their enthalpies of solution being comparable.

| | $Be^{2+}$ | $Mg^{2+}$ | $Ca^{2+}$ | $Sr^{2+}$ | $Ba^{2+}$ | $Ra^{2+}$ | |
|---|---|---|---|---|---|---|---|
| $\bar{S}_i^\circ$ (absolute) | −45 | −18 | −3 | +1 | +13 | +23 | eu. |

The small highly charged ions break up some of the water structure but the overall effect is to produce a more ordered arrangement in solution; the larger species of the same ionic charge result overall in a more random arrangement. Similar changes have been discussed previously with reference to simple halides.[12]

We consider finally the extension of the lattice energy calculations to the selenates. The number of compounds for which adequate crystallographic and thermodynamic data are available is limited to three—silver sulphate, silver selenate and their structure type sodium sulphate. The crystallographic data are taken from WYCKOFF[3] and thermodynamic terms from the sources already discussed.

The lattice energy of sodium sulphate is derived from the Born-Haber cycle, using for $\Delta H_f$ ($SO_4^{2-}$ gas) the value obtained above; the value obtained is −444 kcal/mole. The weighted mean $\bar{r}_0$ value for $Na_2SO_4$ is 3·30(0) Å, from which, taking $\rho = 0{\cdot}35$, we obtain for the constant $A$ in equation (1) the value 4·94. Using this value with the $\bar{r}_0$ value for $Ag_2SO_4$ of 3·44(4) Å we calculate the lattice energy as −428 kcal/mole for this salt. That this is in poor agreement with the corresponding value in Table 1

[15] R. A. ROBINSON, *J. Chem. Soc.* 4543 (1952).

is not surprising since, in general, the lattices of silver salts are considerably more stable than would be inferred from an electrostatic model.

We may therefore use the lattice energy of silver sulphate in Table 1 to deduce an empirical Madelung constant applicable also to silver selenate; the value so obtained is 5·52. With $\bar{r}_0 = 3{\cdot}59(8)$ Å, the lattice energy of silver selenate is $-460$ kcal/mole; inserting this value in equation (2) we obtain $\Delta H_f$ ($SeO_4^{2-}$ gas) $= -120$ kcal/g ion.

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# ELECTRONIC ABSORPTION SPECTRA OF ACETYLACETONATO COMPLEXES—I

## COMPLEXES WITH TRIVALENT TRANSITION METAL IONS

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**Abstract**—The ultra-violet, visible and near infra-red absorption spectra of the following acetylacetonato complexes are reported: $Ti(acac)_3$, $V(acac)_3$, $Cr(acac)_3$, $Mn(acac)_3$, $Fe(acac)_3$, and $Co(acac)_3$.

In this series of complexes the $\pi \rightarrow \pi^*$ transition energy increases with increasing number of $d_\varepsilon$-electrons and this is attributed to metal–ligand $\pi$-interaction. In order to explain the "normal" value of the ligand field splitting parameter $\Delta$, it is proposed that the metal–ligand $\pi$-interaction occurs between $d_\varepsilon$-orbitals of the metal and both higher, empty, $\pi^*$-orbitals and lower, filled, $\pi$-orbitals of the ligands. Other factors affecting the $\pi \rightarrow \pi^*$ transition energy are also discussed.

Electron transfer bands, which are observed in the 300–400 m$\mu$ region, have been assigned to the $d_\varepsilon \rightarrow \pi_4$ transition. The $d_\varepsilon \rightarrow d_\gamma$ transitions are discussed briefly.

In each complex the assignments are discussed in detail. In the case of the $\pi \rightarrow \pi^*$ transition in $Cr(acac)_3$ the assignment differs from that made by previous workers.

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SINCE 1951 a large number of publications have appeared in the literature concerning the interpretation of the absorption spectra of transition metal complexes.[1] Because of the theoretical tool provided by the crystal field theory the greatest success has been with transitions which occur within the *d*-orbitals. Very little work has been done with the intense electron transfer bands and the bands characteristic of the ligand, mainly because of the difficulty in making sufficiently accurate theoretical calculations. However, even the simplest calculations are often useful in studying the absorption spectra of conjugated organic molecules and in the present work naive LCAO-MO calculations were used to help interpret the spectra of a series of acetylacetonato complexes of trivalent transition metal ions. The method of calculation and the numerical results will be presented in a forthcoming paper.[2]

The present work is concerned mainly with the $\pi \rightarrow \pi^*$ transition which is characteristic of the acetylacetonate ion and with the electron transfer transition which appears in each of the complexes in the series $Ti(acac)_3$, $V(acac)_3$, $Cr(acac)_3$, $Mn(acac)_3$, $Fe(acac)_3$, and $Co(acac)_3$. For reasons which are discussed below the electron transfer band is assigned to the $d_\varepsilon \rightarrow \pi_4$ transition and hence involves the transfer of an electron from the metal to the ligand.

## EXPERIMENTAL

With the exception of *tris*(acetylacetonato) titanium(III) all complexes used in this work were prepared by standard methods described in the literature. Analyses are reported in Table 1.

CHAKRAVARTI[3] prepared $Ti(acac)_3$ by passing dry ammonia into a suspension of $TiCl_3$ in dry

[1] Recently reviewed by T. M. DUNN, *Modern Coordination Chemistry* (Edited by J. LEWIS and R. G. WILKINS) Chap. 4, Interscience, New York (1960).
[2] D. W. BARNUM, *J. Inorg. Nucl. Chem.* In press.
[3] B. N. CHAKRAVARTI, *Naturwissenschaften* **45**, 286 (1958).

TABLE 1.—ANALYSIS OF METAL CHELATES

| Complex | Metal (%) | Carbon (%) | Hydrogen (%) |
|---|---|---|---|
| $Sc(C_5H_7O_2)_3$ | — | 52·6(52·6)* | 6·2(6·2) |
| $Ti(C_5H_7O_2)_3$ | 14·2(13·9) | 51·9(52·2) | 6·1(6·1) |
| $V(C_5H_7O_2)_3$ | — | 51·7(51·7) | 6·1(6·1) |
| $Cr(C_5H_7O_2)_3$ | 14·7(14·7) | 52·3(51·6) | 6·3(6·1) |
| $Mn(C_5H_7O_2)_3$ | — | 51·3(51·1) | 6·0(6·0) |
| $Fe(C_5H_7O_2)_3$ | 15·8(15·8) | 51·1(51·0) | 6·0(6·0) |
| $Co(C_5H_7O_2)_3$ | 16·0(16·5) | 50·7(50·6) | 6·0(5·9) |
| $Zn(C_5H_7O_2)_2$ | — | 42·5(45·6) | 5·7(5·4) |

* Values required by theory are given in parentheses

TABLE 2.—ABSORPTION BANDS* IN ACETYLACETONATO COMPLEXES

| Complex | $\lambda_{max}$ (mμ); log ε | | | |
|---|---|---|---|---|
| | Ethanol | Benzene | Chloroform | Dioxane |
| $Sc(acac)_3$ | 296; 4·55 | — | — | — |
| $Ti(acac)_3$ | (240); 3·9 | — | — | (242); 4·0 |
| | (265); 4·0 | — | (267); 4·1 | (265); 4·0 |
| | (280); 4·1 | — | (280); 4·1 | (280); 4·1 |
| | (290); 4·1 | — | (290); 4·1 | (290); 4·1 |
| | 308; 4·30 | 310; 4·32 | 309; 4·29 | 309; 4·28 |
| | 389; 2·84 | 391; 2·92 | 390; 2·88 | 390; 2·89 |
| | (470); 2·6 | (470); 2·8 | (470); 2·8 | (470); 2·8 |
| | (550); 3·0 | (560); 3·1 | (550); 3·1 | (550); 3·1 |
| | 593; 3·18 | 602; 3·27 | 594; 3·22 | 598; 3·24 |
| | (640); 3·0 | (650); 3·1 | (640); 3·1 | (642); 3·1 |
| $V(acac)_3$ | 228; 3·93 | — | — | — |
| | 279; 4·26 | 283; 4·30 | 280; 4·28 | — |
| | 290; 4·26 | 292; 4·30 | 290; 4·28 | — |
| | 343; 3·85 | 348; 3·91 | 345; 3·89 | — |
| | 343; 3·85 | 348; 3·91 | 345; 3·89 | — |
| | (390); 3·1 | — | — | — |
| | (460); 2·4 | (445); 2·6 | (445); 2·5 | — |
| | (550); 1·6 | (540); 1·7 | (535); 1·7 | — |
| $Cr(acac)_3$ | 213; 4·34 | — | — | — |
| | 255; 4·05 | — | 255; 4·06 | 255; 4·04 |
| | 270; 4·02 | — | 272; 4·03 | 273; 4·03 |
| | (295); 3·8 | (297); 3·8 | (298); 3·8 | (290); 3·8 |
| | 332; 4·18 | 337; 4·23 | 336; 4·20 | 335; 4·21 |
| | — | (373); 2·69 | (374); 2·65 | — |
| | 380; 2·63 | 380; 2·69 | 382; 2·66 | 379; 2·66 |
| | 388; 2·63 | 389; 2·69 | 388; 2·65 | 387: 2·65 |
| | (410); 2·2 | (410); 2·2 | (410); 2·2 | — |
| | — | (435); 1·7 | — | (435); 1·7 |
| | 560; 1·82 | 559; 1·80 | 560; 1·82 | 560; 1·83 |

* Bands which appear as shoulders or inflexions on the side of a more intense band are enclosed in parentheses.

TABLE 2. (*Contd.*)

| Complex | $\lambda_{max}$ (mμ); log ε | | | |
|---|---|---|---|---|
| | Ethanol | Benzene | Chloroform | Dioxane |
| $Mn(acac)_3$ | — | — | 272; 4·36 | — |
| | — | 322; 4·00 | 318; 3·96 | — |
| | — | (385); 3·1 | (400); 3·0 | — |
| | — | (445); 2·4 | — | — |
| | — | (550); 2·18 | (550); 2·3 | — |
| | — | — | 1125; 1·93 | — |
| $Fe(acac)_3$ | 235; 4·22 | — | — | 240; 4·26 |
| | 272; 4·44 | — | 273; 4·46 | 273; 4·45 |
| | 351; 3·55 | 353; 3·54 | 353; 3·52 | 353; 3·56 |
| | 431; 3·47 | 434; 3·53 | 437; 3·51 | 434; 3·55 |
| | — | — | 725; 0·5 | — |
| | — | — | 975; 0·2 | — |
| $Co(acac)_3$ | 228; 4·60 | — | — | 229; 4·61 |
| | 256; 4·53 | — | 257; 4·54 | 258; 4·54 |
| | (295); 4·0 | (295); 4·0 | (295); 4·0 | (295); 4·0 |
| | — | — | — | (304); 3·9 |
| | 323; 3·89 | 324; 3·92 | 325; 3·90 | 323; 3·90 |
| | (400); 2·5 | (400); 2·5 | (400); 2·5 | (420); 2·5 |
| | 595; 2·10 | 596; 2·15 | 592; 2·10 | 597; 2·12 |
| | — | — | (800); 0·5 | — |
| | — | — | 1100; 0·28 | — |

benzene and acetylacetone. The precipitate of ammonium chloride that was formed was filtered off and the complex obtained by evaporating the benzene. The following however, is believed to be a more convenient preparation: In a nitrogen atmosphere 10 g (0·10 mole) of purified* Eastman "white label" acetylacetone was dissolved in 40 ml of oxygen-free water by dropwise addition of 6 N ammonium hydroxide and vigorous stirring. About 20 ml of ammonium hydroxide was used. This was added dropwise and with stirring to a solution of 50 ml of water and 25·7 g of a 20 per cent solution of titanium chloride (Fischer Scientific Co.). The titanium trichloride solution first turned red, then blue, and then a blue precipitate of $Ti(acac)_3$ formed. The precipitate was filtered off with suction, washed three times with oxygen-free water, sucked dry, and dried in vacuum over magnesium perchlorate. The dry blue powder was purified in about 1 g amounts by sublimation in vacuum (oil pump) at 140–150°C. The analysis is reported in Table 1. Ebullioscopic determination of the molecular weight in benzene gave 327 (Calc. for $Ti(C_5H_7O_2)_3$, 345·23). The complex is readily oxidized by air.

Absorption spectra were measured by standard methods using a Cary Model 11 or Model 14 recording spectrophotometer. Reagent grade benzene, chloroform and ethanol were used as solvents. 1,4-Dioxane was purified by the method of WEISSBERGER and PROSKAUER.[5] All solvents used for $Ti(acac)_3$ and $V(acac)_3$ were freed from dissolved air by flushing with dry nitrogen for 10–15 min just before use. Also, in measuring the spectra of $Ti(acac)_3$ and $V(acac)_3$ glass stoppered absorption cells with light paths of 0·01, 0·05, 0·10, 0·20 and 0·50 cm were used. These allowed the use of more concentrated solutions and thereby reduced any error due to traces of oxidizing agents in the solvent or air leaks. No oxidation products could be detected in spectra measured in this way.

The observed absorption bands in various solvents are recorded in Table 2.

* Purified by the method of STEINBACH and FREISER.[4]

[4] J. E. STEINBACH and H. FREISER, *Analyt. Chem.* **25**, 881 (1953).
[5] A. WEISSBERGER and E. PROSKAUER, *Organic Solvents*, pp. 139–40. Clarendon Press, Oxford (1935).

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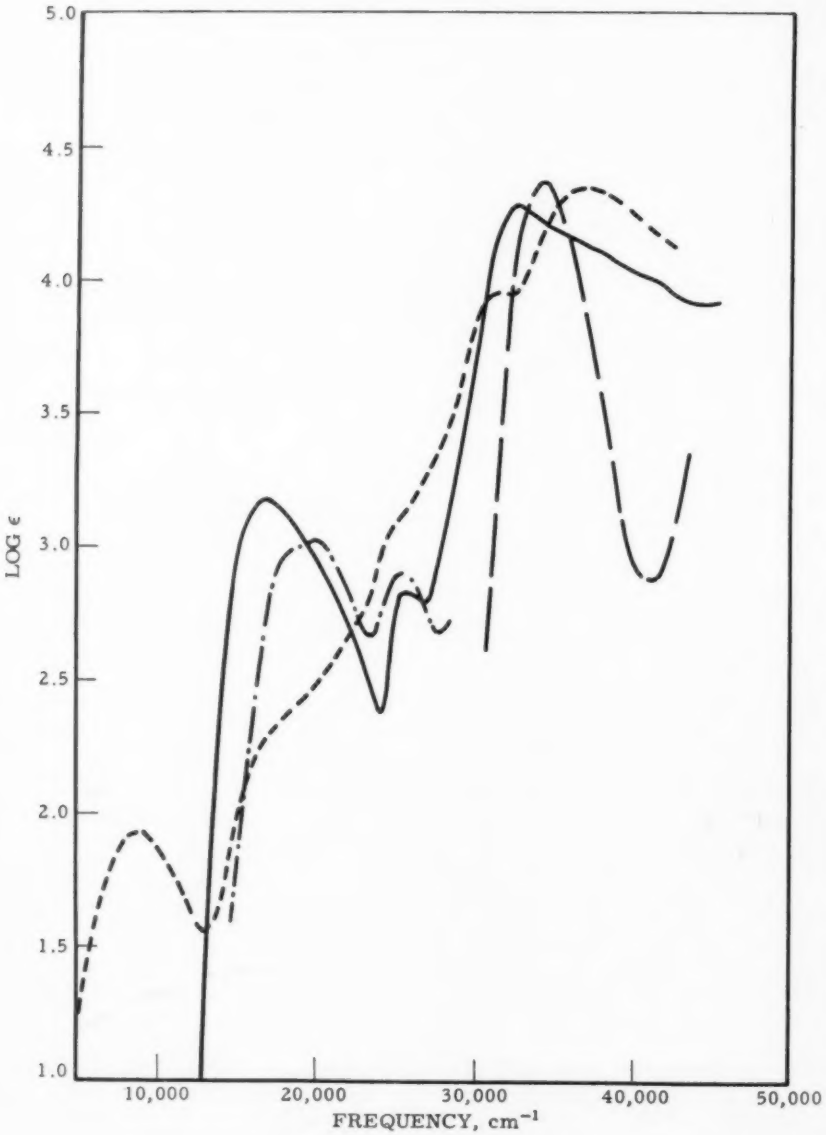


FIG. 1.—Absorption spectra.
——— $Ti(acac)_3$ in ethanol
– – – – $Mn(acac)_3$ in chloroform
— — — Acetylacetone in ethanol, 0·0246 M in $NaOC_2H_5$
–·–·–·– Approximate absorption spectrum of $Ti(acac)_2^+$ in water, pH 3·4

## ASSIGNMENTS

Tris(*acetylacetonato titanium(III)*. The spectrum of $Ti(acac)_3$ (Fig. 1) shows three absorption maxima at 308, 389 and 593 m$\mu$ plus several indistinct shoulders on the 593 m$\mu$ band. The 308 m$\mu$ band is assigned to the $\pi_3 \rightarrow \pi_4$ transition and the 389 m$\mu$ band to the $d_\varepsilon \rightarrow \pi_4$ transition.

The 593 m$\mu$ band is assigned to the $d_\varepsilon \rightarrow d_\gamma$ transition in spite of the fact that it bears no resemblance to the typical pair of bands observed in other titanium(III) complexes.[6–8] Generally, due to Jahn-Teller distortion from regular octahedral symmetry, titanium(III) complexes have two overlapping $d_\varepsilon \rightarrow d_\gamma$ bands which are about 1,000 to 3,000 $cm^{-1}$ apart and have an intensity of about 10 *l.* $mole^{-1}$ $cm^{-1}$. However, in $Ti(acac)_3$ there are at least three shoulders at 635, 555 and 480 m$\mu$ and the intensity at 593 m$\mu$ is 1,520 *l.* $mole^{-1}$ $cm^{-1}$. Very similar absorption bands have been observed in *tris*(benzoylacetonato) titanium(III) and in a blue complex with $\alpha$-picolinic acid. It has been suggested by LIEHR[9] that the shoulders are due to vibrational fine structure.

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Complexes of trivalent titanium are sometimes compared with vanadyl complexes which also have only one 3*d*-electron on the metal ion, and with copper(II) complexes, in which the term splitting is just opposite to that in titanium(III) and vanadium(IV). The strong tetragonal distortion from octahedral symmetry in copper and vanadyl complexes gives rise to three absorption bands rather than one. In both cases the highest energy $d \rightarrow d$ transition usually is observed in the 380–400 m$\mu$ region.[8,10] Therefore, by analogy, one might argue that the 389 m$\mu$ band in $Ti(acac)_3$ is a $d_\varepsilon \rightarrow d_\gamma$ transition that arises from strong tetragonal distortion. LIEHR and BALLHAUSEN[11] have estimated that Jahn-Teller distortion in titanium(III) complexes should result in spectral splittings of approximately 7,000 $cm^{-1}$. The 593 and 389 m$\mu$ bands are 8,800 $cm^{-1}$ apart. Nevertheless, it is believed that such an assignment would be incorrect. In vanadyl and square planar copper complexes the source of strong tetragonal distortion is obvious but there is no apparent reason for such a large distortion in $Ti(acac)_3$ other than that predicted by the Jahn-Teller theorem. It has already been mentioned that this distortion has not been found to exceed about 3,000 $cm^{-1}$ in other titanium(III) complexes. LIEHR himself has stated that the theoretical estimate of the splitting is probably too high.[9] Still better evidence against assigning the 389 m$\mu$ band to a $d_\varepsilon \rightarrow d_\gamma$ transition is that the visible absorption of the 1:2 complex (Fig. 1) consists of two overlapping bands which are typical of $Ti^{3+}$ complexes (the third band is of such low energy that it should lie in the infra-red region). In addition, however, there is a band at 396 m$\mu$ which cannot be a $d \rightarrow d$ transition because these have already been accounted for. Upon going to the 3:1 complex the 396 m$\mu$ band is shifted slightly to 389 m$\mu$, whereas the portion of the spectrum due to the $d \rightarrow d$ transitions changes drastically.

Tris(*acetylacetonato*) *vanadium(III)*. In $V(acac)_3$ there are two overlapping bands at 279 and 290 m$\mu$ (Fig. 2) which have almost identical intensities. It is not known

[6] H. HARTMANN, and H. L. SCHLAFER, *Z. Phys. Chem.* **197**, 116 (1951).
[7] H. HARTMANN, H. L. SCHLAFER and K. H. HANSEN, *Z. Anorg. Chem.* **284**, 153 (1956); 40 (1957).
[8] C. K. JORGENSEN, *Acta Chem. Scand.* **11**, 73 (1957).
[9] A. LIEHR. Private communication (1958).
[10] R. D. FELTHAM, U.S.A.E.C. Report UCRL-3867 (1957).
[11] A. D. LIEHR and C. J. BALLHAUSEN, *Ann. Phys.* **3**, 304 (1958).

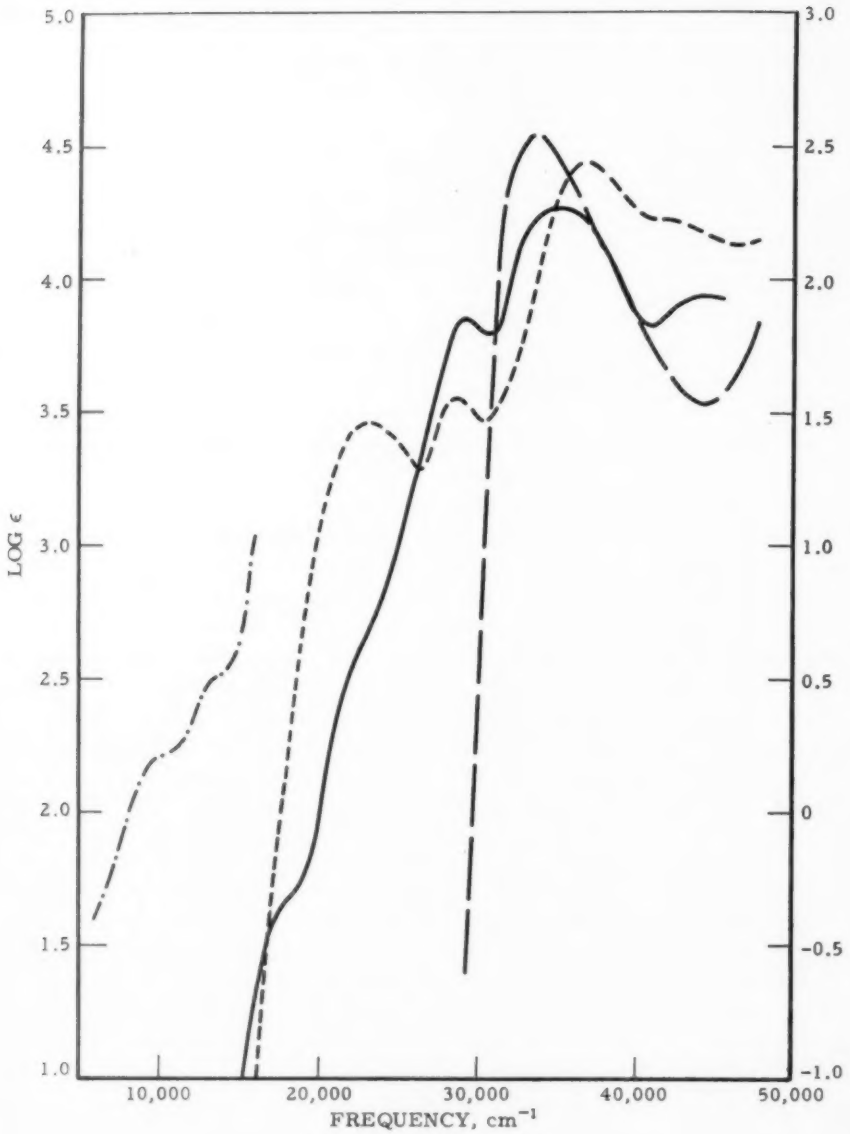


FIG. 2.—Absorption spectra.
——— $V(acac)_3$ in ethanol (left hand scale)
– – – – $Fe(acac)_3$ in ethanol (left hand scale)
— — — $Sc(acac)_3$ in ethanol (left hand scale)
—·—·— $Fe(acac)_3$ in chloroform (right hand scale)

which band is the $\pi_3 \rightarrow \pi_4$ transition, and indeed, they both may be due to this transition, the splitting being due to configuration interaction or perhaps to a splitting of the $\pi_4$-orbitals because of a peculiarity of their symmetry properties. These possibilities are discussed below in more detail. Until this question can be resolved the 290 m$\mu$ band was tentatively assigned to the $\pi_3 \rightarrow \pi_4$ transition.

The 343 m$\mu$ band is assigned to the $d_\varepsilon \rightarrow \pi_4$ transition.

No maxima are observed in the visible region, but there is a shoulder at 550 m$\mu$ which is due to the $^3T_{1_g} \rightarrow {}^3T_{2_g}$ transition and another shoulder at 460 m$\mu$ which is the $^3T_{1_g} \rightarrow {}^3T_{1_g}$(P) transition.

Tris(*acetylacetonato*) *chromium(III)*. Previous investigators have assigned the 332 m$\mu$ band in $Cr(acac)_3$ to the $\pi_3 \rightarrow \pi_4$ transition (Fig. 3), probably on the basis that it is the most intense ultra-violet absorption band. However, upon comparison of this spectrum with those of other complexes, especially $Co(acac)_3$, it was concluded that this band is actually the $d_\varepsilon \rightarrow \pi_4$ transition and that the 270 m$\mu$ band is the $\pi_3 \rightarrow \pi_4$ transition. ORGEL[12] has pointed out that the spectra of chromium(III) and spin paired cobalt(III) complexes are very similar because their ground states and excited states have similar symmetries. Even though the spectra of $Cr(acac)_3$ and $Co(acac)_3$ in Fig. 3 do not appear to be similar at first sight they actually are. The pair of bands at 256 and 228 m$\mu$ in $Co(acac)_3$ corresponds to the 270 and 255 m$\mu$ pair in $Cr(acac)_3$. Both complexes have a shoulder at 295 m$\mu$ and both have an electron transfer band in the same region, i.e., at 332 m$\mu$ in $Cr(acac)_3$ and at 323 m$\mu$ in $Co(acac)_3$. Bands in the visible region are also similar. Now, one would assign the 256 m$\mu$ band in $Co(acac)_3$ to the $\pi_3 \rightarrow \pi_4$ transition, and the corresponding band in $Cr(acac)_3$ lies at 270 m$\mu$. The main difference between the spectra of the cobalt and chromium acetylacetonates is the relative intensities of the bands. In $Cr(acac)_3$ the $d_\varepsilon \rightarrow \pi_4$ transition is unusually intense and the $\pi_3 \rightarrow \pi_4$ transition is unusually weak. A final argument for this assignment is that interpolation between the energies of the electron transfer bands in $V(acac)_3$ and $Mn(acac)_3$ shows that this transition should fall near 332 m$\mu$ in $Cr(acac)_3$.

The $^4A_{2g} \rightarrow {}^4T_{2g}$ transition lies at 560 m$\mu$ and the $^4A_{2g} \rightarrow {}^4T_{1g}$ transition is therefore expected ca. 7,000 $cm^{-1}$ higher,[1,13,14] i.e., at about 400 m$\mu$. A band is observed at 380 m$\mu$ but unlike the "second" band in chromium(III) complexes, it is about seven times more intense than the first band and it shows fine structure. A survey of the published spectra of chromium(III) complexes failed to produce any with a similar band. It is therefore believed that the $^4A_{2g} \rightarrow {}^4T_{1g}$ band is seen as a slight shoulder at 430 m$\mu$ and that the 380 m$\mu$ band is due to some other transition.

Tris(*acetylacetonato*) *manganese(III)*. In ethanolic solution $Mn(acac)_3$ appears to be partly dissociated[15] but not in chloroform or benzene solution.

There is a broad band at 272 m$\mu$ in chloroform which is assigned to the $\pi_3 \rightarrow \pi_4$ transition (Fig. 1). The breadth of the band may be due to a small splitting of the band as already discussed for the case of $V(acac)_3$.

The $d_\varepsilon \rightarrow \pi_4$ transition is clearly distinguishable at 318 m$\mu$.

The shoulder at 550 m$\mu$ is assigned to the $^5E_g \rightarrow {}^5T_{2g}$ transition, which is the only spin allowed $d \rightarrow d$ band expected in an octahedral complex. Actually, $Mn(acac)_3$ is

[12] L. E. ORGEL, *J. Chem. Soc.* 4756 (1952).
[13] L. E. ORGEL, *J. Chem. Phys.* **23**, 1004 (1955).
[14] R. TSUCHIDA, *Bull. Chem. Soc. Japan*, **13**, 388 (1938).
[15] G. H. CARTLEDGE, *J. Amer. Chem. Soc.* **73**, 4416 (1951).

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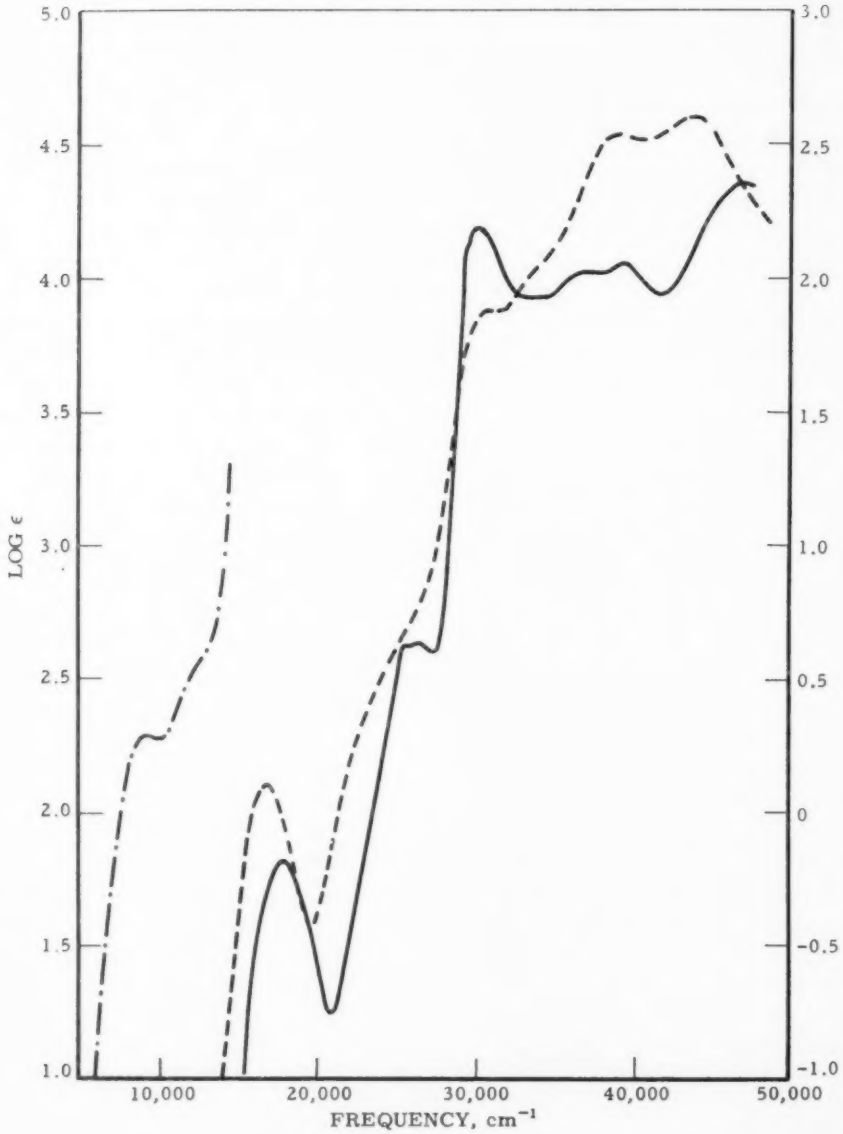


FIG. 3.—Absorption spectra.
——— $Cr(acac)_3$ in ethanol (left hand scale)
— — — $Co(acac)_3$ in ethanol (left hand scale)
–·–·–·– $Co(acac)_3$ in chloroform (right hand scale)

probably distorted to lower symmetry[16,17] but it cannot be detected in this spectrum. The 1125 m$\mu$ band must therefore be the spin forbidden $^5E_g \rightarrow {}^3T_{1g}$ transition, although it has the unusually high intensity of 85·3 *l.* mole$^{-1}$ cm$^{-1}$. FURLANI and CIANA[17] also observed exceptionally intense spin forbidden transitions in some other manganese complexes.

Tris(*acetylacetonato*) *iron*(*III*). The $\pi_3 \rightarrow \pi_4$ transition is located at 272 m$\mu$ and the $d_\varepsilon \rightarrow \pi_4$ transition at 351 m$\mu$ (Fig. 2). The unusually low energy of the electron transfer band is due to the exceptionally small splitting of the 3*d*-orbitals by the ligand field in a spin-free iron(III) complex, and will be discussed in a forthcoming report.[2] The origin of the band at 431 m$\mu$ is unknown.

In chloroform, two weak spin-forbidden bands were observed at 725 and 975 m$\mu$. These are the $^6A_{1g} \rightarrow {}^4T_{2g}$ and the $^6A_{1g} \rightarrow {}^4T_{1g}$ transitions, respectively.

Tris(*acetylacetonato*) *cobalt*(*III*). The ultra-violet spectrum of Co(acac)$_3$ has already been discussed in connection with the spectrum of Cr(acac)$_3$.

In chloroform solution, two weak shoulders were observed at 1100 and 800 m$\mu$ (Fig. 3). These are assigned respectively to the spin forbidden transitions $^1A_{1g} \rightarrow {}^3T_{1g}$ and $^1A_{1g} \rightarrow {}^3T_{2g}$.

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## $\pi \rightarrow \pi^*$ TRANSITIONS

The enol form of acetylacetone (the hydrogen chelate) has an intense absorption band which appears at 272–274 m$\mu$ (log $\varepsilon \sim 4{\cdot}0$) in a number of different solvents. In basic solution the enolate ion is formed, the absorption band shifts to 294 m$\mu$ (Fig. 1), and the intensity increases slightly.[18] The $\pi$-energy level diagram of the enolate ion, which was obtained from a Hückel LCAO–MO calculation,[2] is shown in Fig. 4, and the 294 m$\mu$ band is assigned to the $\pi_3 \rightarrow \pi_4$ transition.[19–21]

Upon chelation with a metal ion the $\pi \rightarrow \pi^*$ transition may shift either to longer or to shorter wavelength with respect to the enolate ion. Attempts have been made by previous authors to correlate this shift with some property of the metal ion, the structure of the complex, the nature of the metal–ligand bonds, or the formation constants.[19,22,23,24] In the most recent and complete study HOLM and COTTON[20] measured the spectra of a large number of complexes and concluded that several factors, which cannot be easily separated, contribute to the position of this band. Although this difficulty has not been resolved in the present work, it has been found that the effect of metal–ligand $\pi$-interaction in the trivalent transition metal complexes is large enough that it stands out over the other effects.

*Valence bond considerations.* BASU and CHATTERJI[22] observed that in some acetylacetonato complexes there are two intense ultra-violet absorption bands rather than one. They first assumed that these two bands indicate that the two C=O bonds (and consequently the two metal–oxygen bonds) in a chelate ring are different. In a more recent paper[23] they apparently abandon this view and assume instead that upon chelation the 274 m$\mu$ band of the enol form of acetylacetone splits into two

[16] A. FORMAN and L. E. ORGEL, *Mol. Phys.* **2**, 362 (1959).
[17] C. FURLANI and A. CIANA, *Ann. Chim.* (Rome) **48**, 286 (1958).
[18] E. E. BLOUT, V. W. EAGER and D. C. SILVERMAN, *J. Amer. Chem. Soc.* **68**, 566 (1946).
[19] R. L. BELFORD, A. E. MARTELL and M. CALVIN, *J. Inorg. Nucl. Chem.*, **2**, 11, (1956).
[20] R. H. HOLM and F. A. COTTON, *J. Amer. Chem. Soc.* **80**, 5658 (1958).
[21] E. L. ZEBROSKI, U.S.A.E.C. Report BC-63
[22] S. BASU and K. K. CHATTERJI, *Naturwissenschaften.* **42**, 413 (1955); **43**, 124 (1956).
[23] S. BASU and K. K. CHATTERJI, *Z. Phys. Chem.* **209**, 360 (1958).
[24] A. I. KISS and J. CSASZAR, *Acta Chim. Acad. Sci. Hung.* **13**, 49 (1957).

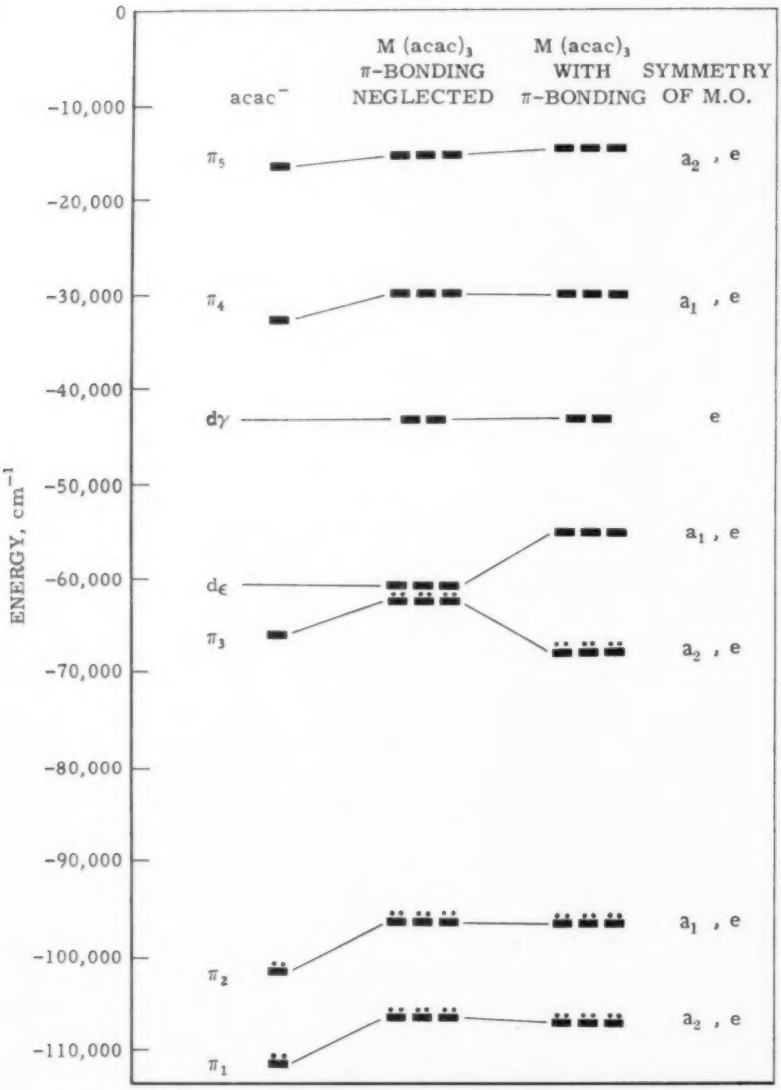
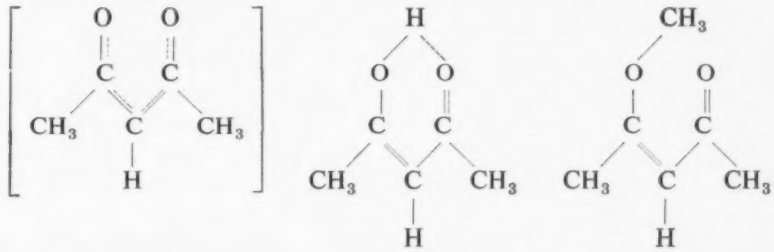



FIG. 4.—Molecular orbitals of the acetylacetonate anion and of a trivalent transition metal complex.

bands. One band shifts to lower wavelength if the metal–oxygen bond is more covalent than the hydrogen–oxygen bond in the enol. This is illustrated in the series enolate, enol, and O-methyl ether of acetylacetone shown below. The second band was assumed to be due to metal–ligand $\pi$-bonding, and it was further assumed that it shifts to lower energy since $\pi$-bonding results in an increase in the length of the conjugated system. It has since been shown that this assumption is incorrect. That is, metal-ligand $\pi$-bonding results in a shift of the $\pi \rightarrow \pi^*$ transition to *higher* energy.[2]

Furthermore, the splitting of an absorption band into two new bands implies a splitting of the excited state by configuration interaction or by the symmetry properties of the atomic orbitals which are combined in the complex. It does not seem likely that such phenomena can be explained on the basis of valence bond structures.

*Equivalence of metal–oxygen bonds.* If the two metal–oxygen bonds in a chelate ring were *not* equivalent it can be calculated that the $\pi \rightarrow \pi^*$ transition would be shifted as much as 4,000 $cm^{-1}$ to higher energy (from 294 m$\mu$ to 263 m$\mu$) due to loss of delocalization energy. This is believed to be the reason why the enol form of acetylacetone has maximum absorption 2,700 $cm^{-1}$ above that of the enolate ion. That is, the hydrogen bond is not symmetrical and therefore the two C=O and C=C bonds in the ring are not equivalent. The loss of delocalization energy and the resulting shift to higher energy can be seen in the following series of compounds:



$\nu_{max} = 34{,}000\ cm^{-1}$ $\nu_{max} = 36{,}600\ cm^{-1}$ $\nu_{max} = 39{,}300\ cm^{-1}$ (25)

KEUSSLER and ROSSMY[25] observed that the deuterated enol shows maximum absorption very close to that of the hydrogen complex (37,000 $cm^{-1}$), and interpreted this to mean that the hydrogen atom lies in a potential well with only a very small barrier between the two minima, since resonance in the enol would require that the proton change its position by tunneling through any potential barrier. However, in the interpretation presented here one would not expect a large difference between the $\pi_3 \rightarrow \pi_4$ transition energies in the hydrogen and dueterium chelates since the loss in delocalization energy should be about the same in both cases.

In other chelates, however, structure determinations by X-ray diffraction have shown that, within experimental error, the metal-oxygen bonds are equivalent.[26] Therefore, except for the hydrogen chelate, non-equivalence of these bonds is not expected to be a factor which influences the ultra-violet absorption spectrum.

[25] V. KEUSSLER and G. ROSSMY, *Z. Elektrochem.* **60**, 136 (1956).

[26] V. AMIRTHALINGAM, V. M. PADMANABHAN and J. SHANKAR, *Acta Cryst.* **13**, 201 (1960); G. J. BULLEN, *Acta Cryst.* **12**, 703, (1959); R. P. DODGE, U.S.A.E.C. Report UCRL-8225 (1958); H. KOYAMA, Y. SAITO and J. KUROYA, *Inst. Polytech. Osaka City Univ.* Ser. C, **4**, 43 (1953), *Chem. Abstr.*, **48**, 3097 b; V. M. PADMANABHAN, *Proc. Indian Acad. Sci.* **47**A, 329 (1958); R. B. ROOF JR., *Acta Cryst.* **9**, 781 (1956); E. A. SHUGAM, *Trudy Vsesoyuz. Nauch. -Issledovatel. Inst. Khim. Reaktivov* No. 21, 108–11 (1956), *Chem. Abstr.* **53**, 21025 g; J. V. SILVERTON and J. L. HOARD, *Abstracts of Papers, Amer. Chem. Soc. Meeting*, Div. of Phys. Chem. Sept. 11–16, (1960).

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*Effect of positive charge on the metal ion.* BELFORD *et al.*[19] made a Hückel LCAO-MO calculation of the atomic charges in the ground state and the excited state of the acetylacetonate ion and then calculated, on the basis of the coulomb forces, the change in energy of both of these states which is brought about by placing a point positive charge in the position of the metal ion. They found that an increase of one unit in positive charge should shift the $\pi \rightarrow \pi^*$ transition about 3,200 $cm^{-1}$ to lower energy, but HOLM and COTTON[20] have shown that such a shift is seldom observed, even in some especially favourable cases in which the metal–ligand bonding is apparently "ionic" and the sizes of the metal ions of charge +1 and +2 which were compared were about equal. The calculation itself appears to be valid, however, since it correctly predicts the effect of a positively charged quaternary nitrogen atom on the $\pi \rightarrow \pi^*$ transition in some $\alpha,\beta$-unsaturated ketones[27] and SCHLÄFER and KÖNIG[28,29] have used essentially the same method to predict the effect of metal ions on the $\pi \rightarrow \pi^*$ transitions in pyridine and 1,10-phenanthroline complexes.

Actually, metal–ligand bonds are neither 100 per cent ionic nor 100 per cent covalent[1,30,31] and the charge on the metal ion is less than the formal charge. Pauling's electronegativity values were used to estimate the amount of covalent character, and hence the actual charge on the metal on, but this did not lead to any improvement in the correlation between positive charge and transition energy.

*Effect of metal–ligand $\pi$-bonding.* In Fig. 4 the calculated energy level diagram of the free acetylacetonate ion is shown with its six $\pi$-electrons in the $\pi_1$, $\pi_2$ and $\pi_3$-orbitals. When this ion complexes with a metal the MO calculations show that the $\pi$-orbitals are all raised slightly in energy and the $d_\varepsilon$ and $d_\gamma$-orbitals fall in between the $\pi_3$ and $\pi_4$-orbitals. These calculations and the order of the energy levels are discussed in a forthcoming paper.[2] In the ground state the appropriate number of electrons are distributed in the molecular orbitals according to Hund's rules and with the additional stipulation that if there are between four and seven 3*d*-electrons, and if the $d_\varepsilon$ and $d_\gamma$-orbitals are close enough together, it may cost less energy to put the last electrons into the $d_\gamma$-orbitals rather than pairing them with electrons already in the $d_\varepsilon$-orbitals. That is, the ground state is the spin free configuration rather than the spin paired.[32] The electronic configurations found by magnetic susceptibility measurements are given in Table 3.

As seen in Fig. 4 the LCAO-MO calculations show that the effect of metal-ligand $\pi$-interaction is to shift the $\pi_3 \rightarrow \pi_4$ transition to higher energy. Previous investigators have assumed that this transition will shift to lower energy since an increase in metal–ligand $\pi$-bonding involves an increase in the length of the resonance path. However, this rule applies only to transitions from the highest occupied $\pi$-orbital to the lowest unoccupied $\pi^*$-orbital, and even then there are exceptions.[37] Since the $d_\varepsilon$-orbitals, which are the ones that participate in double bonding with the ligands, lie in between the $\pi_3$ and the $\pi_4$-orbitals, the $d_\varepsilon$-orbitals become the highest occupied "$\pi$-orbitals". The effect of inserting a new $\pi$-orbital in between two others is to spread them apart, shifting the electronic transition between them to higher energy.

[27] D. W. BARNUM. To be published.
[28] H. L. SCHLÄFER, *Z. Phys. Chem.* **8**, 373 (1956).
[29] H. L. SCHLÄFER, and E. KÖNIG, *Z. Phys. Chem.* **19**, 265 (1959).
[30] C. K. JORGENSEN, *Acta Chem. Scand.*, **12**, 903 (1958); *Disc. Faraday Soc.* 110 (1958).
[31] W. LOW, *Paramagnetic Resonance in Solids*, p. 96. Academic Press, New York and London (1960).
[32] L. E. SUTTON, *J. Inorg. Nucl. Chem.* **8**, 23 (1958); *J. Chem. Educ.* **37**, 498 (1960).

Now, there are two types of $\pi$-interaction. In the first type, which is illustrated in Fig. 5a, the $d_\varepsilon$-orbitals interact with higher energy, empty, anti-bonding $\pi$-orbitals of the ligand. This leads to increased stability by lowering the energy of $d_\varepsilon$-electrons and decreasing the coulomb repulsion between the $d_\varepsilon$-electrons by allowing them to spread out over the ligands. Partial donation of $d_\varepsilon$-electrons to the ligands also enhances the donation of $\sigma$-electrons from the ligand to the metal ion. Since the

TABLE 3.—ELECTRONIC CONFIGURATIONS IN SOME ACETYLACETONATO COMPLEXES

| Complex | No. of 3*d*-electrons | Config. | Ref. | $\nu$ max., $\pi \rightarrow \pi^*$ ($cm^{-1}$) |
|---|---|---|---|---|
| $Sc(acac)_3$ | 0 | $d_\varepsilon^0$ | — | 33,800 |
| $Ti(acac)_3$ | 1 | $d_\varepsilon^1$ | — | 32,500 |
| $V(acac)_3$ | 2 | $d_\varepsilon^2$ | — | 34,500 |
| $Cr(acac)_3$ | 3 | $d_\varepsilon^3$ | 33 | 37,100 |
| $Mn(acac)_3$ | 4 | $d_\varepsilon^3 d_\gamma^1$ | 33, 34 | 36,800 |
| $Fe(acac)_3$ | 5 | $d_\varepsilon^3 d_\gamma^2$ | 35 | 36,800 |
| $Co(acac)_3$ | 6 | $d_\varepsilon^6$ | 33, 36 | 39,100 |

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energy of the $d_\varepsilon$-electrons is decreased the value of $\Delta$, the energy difference between the $d_\varepsilon$ and the $d_\gamma$-orbitals, is increased, Therefore, complexes which have this type of $\pi$-bonding have unusally high energy $d \rightarrow d$ absorption bands.

In the second type of $\pi$-interaction, shown in Fig. 5b, the $d_\varepsilon$-orbitals interact with lower energy, filled, $\pi$-orbitals of the ligands. This lowers the energy of the ligand $\pi$-orbitals but at the same time it raises the energy of any $d_\varepsilon$-electrons, and hence decreases the value of $\Delta$. If the $d_\varepsilon$-orbitals are filled, as in $Co(acac)_3$, there is no net gain in electronic energy since six electrons have been lowered and six have been raised. In fact, an increase in energy is expected due to the coulomb repulsion between the $d_\varepsilon$-electrons and the $\pi$-electrons on the ligands. Furthermore, in this type of $\pi$-interaction, $\pi$-electrons are transferred from the ligand to the metal and they are therefore competing with the ligand $\sigma$-electrons for the quota of electron density that the metal ion can accept.

The acetylacetonate ion has an empty $\pi_4$-orbital, above the $d_\varepsilon$-orbital, but it also has a filled $\pi_3$-orbital which is lower than the $d_\varepsilon$-orbital. Thus, both types of $\pi$-interaction discussed above seem possible. The Hückel LCAO-MO calculations show that the $\pi_3$-orbitals are depressed and the $\pi_4$-orbitals remain unaffected by $\pi$-interaction, suggesting that the interaction is of the second type.

The literature contains contradictory remarks about the amount of $\pi$-bonding in acetylacetonato complexes. NAKAMOTO and MARTELL[38] concluded from the infrared absorption spectrum and a normal coordinate treatment of $Cu(acac)_2$ that the metal ligand bonding is intermediate between that found in $Ni(CO)_4$ and in $Fe(CN)_6^{4-}$, two species in which it is believed to be quite strong. This is in agreement with a

[33] H. S. JARRETT, *J. Chem. Phys.* **27,** 1298 (1957).
[34] L. C. JACKSON, *Proc. Roy. Soc.* **47,** 1029 (1935).
[35] L. C. JACKSON, *Proc. Roy. Soc.* A **140,** 695 (1933).
[36] R. O. WHIPPLE, R. WEST and K. EMERSON, *J. Chem. Soc.* 3715 (1953).
[37] A. PULLMAN and B. PULLMAN, *Disc. Faraday Soc.* **9,** 46 (1950).
[38] K. NAKAMOTO and A. MARTELL, *J. Chem. Phys.* **32,** 588 (1960).

statement made by McGARVEY[39] but in a subsequent paper MAKI and McGARVEY[40] conclude from paramagnetic resonance data that in $Cu(acac)_2$ " . . . the out-of-plane $\pi$-bonding is ionic". The position of the $\pi_3 \rightarrow \pi_4$ transition in $Cu(acac)_2$ supports this latter conclusion.

As for other acetylacetonato complexes, another argument against the existence of strong metal-ligand $\pi$-bonding is the position of the acetylacetonate ion in the spectrochemical series.[41] Those ligands which are known to form strong $\pi$-bonds

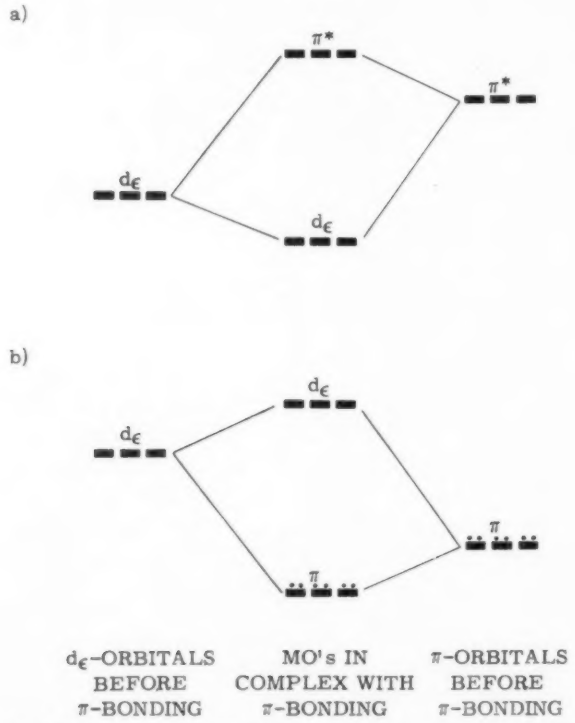


FIG. 5.—Effect of different types of metal–ligand $\pi$-bonding on the energy of the $d_\varepsilon$ and $\pi$-orbitals. (a) Empty $\pi$-orbitals of higher energy than the $d_\varepsilon$-orbitals. (b) Full $\pi$-orbitals of lower energy than the $d_\varepsilon$-orbitals.

of the first type, such as $CN^-$, $NO_2^-$, and 1,10-phenanthroline, have unusually high positions in this series. Ligands which give rise to $\pi$-interaction of the second type, such as the halides, lie somewhat low in the series. The acetylacetonate ion, however, has an intermediate position, very close to that of water, and this indicates that $\pi$-interaction is not strong.

On the other hand, the $\pi_3 \rightarrow \pi_4$ transition energies indicate strong $\pi$-interaction in some complexes. In Table 4 it can be seen that the energy varies over a range of 6,500 $cm^{-1}$ (from 308 m$\mu$ to 256 m$\mu$). It does not seem likely that some simple property of the metal ion such as the electronegativity or charge/radius ratio could cause such a large spread. The direction of the shift suggests that $\pi$-interaction is

[39] B. R. McGARVEY, *J. Phys. Chem.* **60**, 71 (1956).
[40] A. H. MAKI and B. R. McGARVEY, *J. Chem. Phys.* **29**, 31 (1958).
[41] V. SHIMURA and R. TSUCHIDA, *Bull. Chem. Soc. Japan*, **29**, 311 (1956).

increasing as one goes through the series from $Ti(acac)_3$ to $Co(acac)_3$. In fact, as can be seen in Table 4, the wavelength of the $\pi_3 \rightarrow \pi_4$ transition depends on the number of $d_\varepsilon$-electrons. The $d_\varepsilon$-electrons are the ones which satisfy the symmetry requirements for combining with the ligand $\pi$-molecular orbitals.

In order to explain these observations it is suggested that the actual $\pi$-interaction in acetylacetonato complexes is a combination of the two different types described above. Thus, the $d_\varepsilon$-orbitals interact with both lower, filled $\pi$-orbitals and the higher, empty $\pi$-orbitals. This has the effect of spreading the $\pi_3$ and $\pi_4$-orbitals apart and shifting the transition between them to higher energy. At the same time, $\pi$-interaction of the first type tends to lower the energy of the $d_\varepsilon$-orbitals, but interaction of the

TABLE 4.—OBSERVED ENERGIES OF $\pi_3 \rightarrow \pi_4$ AND $d_\varepsilon \rightarrow \pi_4$ TRANSITIONS

| Complex | Number of $3d_\varepsilon$-electrons | $\pi_3 \rightarrow \pi_4$, ($cm^{-1}$) | $d_\varepsilon \rightarrow \pi_4$, ($cm^{-1}$) |
|---|---|---|---|
| $Sc(acac)_3$ | 0 | 33,800 | none |
| $Ti(acac)_3$ | 1 | 32,600 | 25,700 |
| $V(acac)_3$ | 2 | 34,500 | 29,200 |
| | | 35,900?* | |
| $Cr(acac)_3$ | 3 | 37,100 | 30,200 |
| | | 39,200? | |
| $Mn(acac)_3$† | 3 | 36,800 | 31,400 |
| $Fe(acac)_3$ | 3 | 36,800 | 28,500 |
| $Co(acac)_3$ | 6 | 39,100 | 31,000 |
| | | 43,900? | |

* Bands followed by a question mark (?) are due to apparent splitting of the $\pi_3 \rightarrow \pi_4$ transition, as discussed in the text. Solvent is absolute ethanol unless stated otherwise.

† Chloroform solution.

second type tends to raise their energy. The net result is that the energy of the $d_\varepsilon$-orbitals and hence the vaue of $\Delta$, remains about the same as if no $\pi$-interaction were present. Both types of $\pi$-interaction depend strongly on the number of $d_\varepsilon$-electrons, the first type because it lowers the energy of these electrons and there are more electrons available to transfer charge back to the ligands, the second type because the interelectronic repulsion increases with increasing number of $d_\varepsilon$-electrons.

In the acetylacetonato complexes of divalent transition metal ions the $\pi_3 \rightarrow \pi_4$ transition energy is very close to that of the free acetylacetonate anion. This indicates that $\pi$-interaction is not strong, in agreement with the paramagnetic resonance studies of MAKI and MCGARVEY[40] on $Cu(acac)_2$. In the chelates of $Ni(acac)_2$, $Cu(acac)_2$, and $Zn(acac)_2$ the $d_\pi$-orbitals are full, and by analogy with $Co(acac)_3$ one might expect strong $\pi$-interaction in these complexes as well. Although certain rationalizations might be made, this is not yet understood. It is a further reminder, however, that other factors are of importance besides the number of $d_\varepsilon$-electrons. Apparently, in the above series of trivalent transition metal complexes the effect of $\pi$-interaction is large enough that it overshadows these other effects. It would be naive to assume that these other effects were even nearly constant upon going through the series since $Sc(acac)_3$ does not fall in order with the rest of the series, and even in the series $Be(acac)_2$, $Mg(acac)_2$, $Ca(acac)_2$, $Sr(acac)_2$, and $Ba(acac)_2$, the position of the $\pi_3 \rightarrow \pi_4$ transition shows no regular trend.[20]

*Configuration interaction.* The effect of coulomb repulsion between electrons

(configuration interaction) is neglected in the Hückel LCAO-MO model. This interaction often causes an absorption band which involves degenerate orbitals in either the ground state or the excited state to split into two or more bands as, for example, in benzene.[42] It is important to inquire into the possibility of such splitting in the absorption spectra of metal chelates.

Even though the $\pi_\varepsilon$-orbitals in a $M(acac)_3$ complex are triply degenerate (Fig. 4), each of the three pair of electrons is on a separate chelate ring. Since they are so far apart the repulsion between them, and hence the magnitude of any splitting of the $\pi_3 \rightarrow \pi_4$ absorption band is expected to be much smaller than in benzene where the degenerate orbitals are on the same ring. With increasing metal–ligand $\pi$-interaction the repulsion between electrons in different rings should increase. This may be the reason for the apparent splitting of the $\pi_3 \rightarrow \pi_4$ transition that is often observed. For example, in $Cu(acac)_2$, $Al(acac)_3$, $Th(acac)_4$, and many other complexes in which $\pi$-interaction is very weak if it occurs at all, a slight shoulder appears on the long wavelength side of the $\pi_3 \rightarrow \pi_4$ band. However, in the complexes with trivalent transition metal ions the splitting is even more distinct and appears to increase with increasing number of $d_\varepsilon$-electrons. In $V(acac)_3$ there are two distinct humps with approximately equal intensity in the $\pi_3 \rightarrow \pi_4$ region. Similarly, in $Cr(acac)_3$ and $Co(acac)_3$ there are two close bands that might be attributed to configuration interaction. These bands are listed in Table 4. Even though the splitting is appreciable, it is still small with respect to that observed in benzene.

There is another possible explanation for the apparent splitting of the $\pi_3 \rightarrow \pi_4$ band. Since the $d_\varepsilon$-orbitals belong to the $a_1$ and $e$ representations of $D_3$ they may interact with $\pi$-orbitals on the ligands which belong to $a_1$ or $e$ but not to the $a_2$ representation. The Hückel LCAO-MO calculations do not predict an interaction with the $\pi_4$-orbitals, but a more elaborate treatment may show that the $\pi_4(e)$-orbitals are raised in energy by $\pi$-interaction while the $\pi_4(a_2)$-orbitals remain unaffected. Thus, the $\pi_4$-orbitals would be split by $\pi$-bonding and, just as observed in the ultraviolet spectra, the splitting would increase with increasing metal-ligand $\pi$-interaction.

## ELECTRON TRANSFER TRANSITIONS

The trivalent transition metal acetylacetonates studied in the present work have an absorption band between 300 and 400 m$\mu$ which is characteristic of neither the metal ion nor the ligand. The intensities are on the order of 1,000 to 10,000 *l.* mole$^{-1}$ cm$^{-1}$. From the results of the MO calculations and the direction of shift upon going through this series of complexes these bands are assigned to the $d_\varepsilon \rightarrow \pi_4$ transition.

In Fig. 4 it can be seen that there are several possible one electron transitions that involve both an orbital which is principally on the metal and an orbital which is principally on the ligand, and which have energies less than 50,000 cm$^{-1}$. Certain of these are not possible in specific cases. For example, transitions to the $d_\varepsilon$-orbitals

$$\left.\begin{array}{l}\pi_3 \rightarrow d_\varepsilon \\ \pi_3 \rightarrow d_\gamma \\ \pi_2 \rightarrow d_\varepsilon \\ n \rightarrow d_\varepsilon \\ n \rightarrow d_\gamma\end{array}\right\} \text{Electron transfer from ligand to metal} \qquad \left.\begin{array}{l}d_\varepsilon \rightarrow \pi_4 \\ d_\varepsilon \rightarrow \pi_5 \\ d_\gamma \rightarrow \pi_4 \\ d_\gamma \rightarrow \pi_5\end{array}\right\} \text{Electron transfer from metal to ligand}$$

[42] F. A. MATSEN, *Chemical Applications of Spectroscopy*, (Edited by W. WERT) Part 2, Chap. 5, p. 667. Interscience, New York (1956).

are not possible in $Co(acac)_3$ since they are already filled. Similarly, transitions from the $d_\gamma$-orbitals are only possible in $Mn(acac)_3$ and $Fe(acac)_3$ because these are the only complexes which have electrons in the $d_\gamma$-orbitals in the ground state.

The trivalent metal ions of Ti, V, Cr, Mn, Fe, and Co become more difficult to oxidize on going through this series. With the exception of $Fe(acac)_3$, the observed electron transfer bands shift to higher energy on going through the series $Ti(acac)_3$, $V(acac)_3$, $Cr(acac)_3$, $Mn(acac)_3$, $Fe(acac)_3$, and $Co(acac)_3$ (Table 4). Therefore the transition must involve "oxidation" of the central metal ion. That is, the electron is transferred from the metal to the ligand, and it is assigned to the $d_\varepsilon \rightarrow \pi_4$ rather than to the $d_\varepsilon \rightarrow \pi_5$ transition on the basis of the calculated energy differences between these orbitals.

*Note added in proof*—FERGUSON has concluded from an analysis of the polarization of absorption bands in the crystal spectrum of $Cu(acac)_2$ that metal-ligand $\pi$-bonding is strong [*J. Chem. Phys.* **34,** 1609 (1961)]. He also points out that the conclusion from paramagnetic resonance studies that the $\pi$-bonding is "ionic"[40] depended on an erroneous assignment of the $d \rightarrow d$ transitions. This conclusion is not necessarily at variance with the U.V. absorption spectrum of $Cu(acac)_2$ since more complete MO calculations[2] for $M(acac)_3$ complexes have shown that the $\pi_3 \rightarrow \pi_4$ transition is split into four transitions by $\pi$-bonding. One transition is independent of metal-ligand $\pi$-bonding and the other three shift to higher energy. A similar splitting is expected in the $M(acac)_2$ case. Thus, the 295 m$\mu$ band of $Cu(acac)_2$ is probably a $\pi_3 \rightarrow \pi_4$ transition that is independent of $\pi$-bonding. A band is also observed at 242 m$\mu$ which may be a $\pi_3 \rightarrow \pi_4$ transition that is shifted to higher energy by $\pi$-bonding.

CHARETTE *et al.* [*J. Phys. Chem.* **65,** 735 (1961)] arrived at the opposite conclusion from this author regarding the equivalence of the two C=O and the two C=C bonds in a chelate ring. Although these bonds are not equivalent in the copper(II) tropolone complex they are equivalent, within experimental error, in all acetylacetonato complexes for which X-ray structure determinations have been carried out.[26] Actually, these workers made an error in the calculation of the absorption maximum and the value refers to the enolate anion rather than the enol. With a smooth potential well the correct value should be 314 m$\mu$, which is in fair agreement with the observed value of 295 m$\mu$. It is therefore not necessary to assume that the pairs of C=O and C=C bonds are not equivalent.

*Acknowledgements*—The author is indebted to Dr. D. P. STEVENSON and Dr. J. D. SWALEN for many helpful discussions and suggestions.

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# THE INFRA-RED SPECTRA AND STRUCTURES OF SOME HYDRATED URANIUM TRIOXIDES AND AMMONIUM DIURANATES

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**Abstract**—The infra-red spectra of $UO_4$, $2H_2O$; $UO_3$, $2H_2O$; $UO_3$, $1H_2O$; $UO_3$, $0{\cdot}8H_2O$ and $UO_3$ are shown, together with those of $UO_3$, $2D_2O$ and $UO_3$, $0{\cdot}8D_2O$. The principal bands have been assigned and some conclusions drawn concerning the structure. An empirical relationship between $\nu_{OH}$, $\delta_{OH}$ and $\nu_{UO}$ frequencies is shown. The infra-red spectra of a number of samples of ammonium diuranate have also been examined. Two of these samples have been shown by detailed comparison with the spectra of the $UO_3$ hydrates to be in the form $UO_2(OH)_2.xNH_3.yH_2O$, and the spectra of other samples are also consistent with this structure. The composition is very variable and chemical analysis has been performed on some of the samples; these results are included.

THE product known as ammonium diuranate (ADU) has a very variable composition which depends upon the method of preparation, and a number of samples of this product were examined in an attempt to elucidate both the structure and variations in the latter. It became obvious after a study of the spectra that the structure was closely related to that of the $UO_3$ hydrates, and some of these have been studied in order to assist in assigning a number of the infra-red bands.

Two of the ADU's studied proved amenable to an analysis of the structure based on the results of the examination of the hydrated oxides, and this paper deals mainly with these, but the spectra of other samples show that they also have similar structures.

## EXPERIMENTAL

### *Materials*

The nomenclature and methods of preparation of the $UO_3$ hydrates are based on those described by DAWSON *et al.*[1] $UO_4.2H_2O$ was prepared by precipitation from uranyl nitrate solution with hydrogen peroxide. The sample was filtered off and dried at 30°C, a further portion being dried at 110°C for 2 hr. Amorphous $UO_3$ was obtained by heating $UO_4.2H_2O$ at 280°C for 3 hr. The $UO_3$ sample was divided into two portions and each was stood in a desiccator in contact with the vapour over $H_2O$ and $D_2O$ respectively. Overnight both samples turned from the orange red colour of $UO_3$ to the bright yellow of the dihydrate, but the samples were left in contact with the vapour for a period of five weeks. Spectra of $UO_3.2H_2O$ (Sample A) and $UO_3.2D_2O$ were obtained immediately after the samples were removed from the desiccators, and the identity of the $UO_3.2D_2O$ was confirmed by X-ray analysis. $UO_3.0{\cdot}8H_2O$ and $UO_3.0{\cdot}8D_2O$ were obtained from the corresponding dihydrates by heating in a closed vessel of about 1 l. capacity for 18 hr at 155°C; the identity of the latter was checked by X-ray analysis. The sample of $UO_3.1{\cdot}0H_2O$ and two samples of $UO_3.2H_2O$ (J1 and W11, the latter having higher crystallinity) were supplied by Dr. WAIT. The deuterated form of (W11) was obtained by standing a few milligrams of crystals in contact with the vapour over $D_2O$ for 18 hr; deuteration was of the order of 90 per cent as measured from the spectra.

Several ammonium diuranates from different sources were examined. The reference numbers of these and their origins are shown in Table 1. Several of these samples were analysed by Mr. J. WALKDEN at Chatham, with the results shown in Table 2. The analyses were performed after drying at 105° as

[1] J. K. DAWSON, E. WAIT, K. ALCOCK and D. R. CHILTON, *J. Chem. Soc.* 3531 (1956).

TABLE 1.—NOMENCLATURE OF ADU SAMPLES EXAMINED AND THEIR METHOD OF PREPARATION

| Designation | Origin | X-ray pattern | Analysis |
|---|---|---|---|
| ADU "C" | Laboratory stock. History unknown. | Type 1 | Yes |
| ADU 1 | *Continuous precipitation pH 8·0 | Type 2‡ | Yes |
| ADU 2 | *Continuous precipitation pH 4·5 | Type 2 | Yes |
| ADU 3 | *Continuous precipitation pH 7·3 | | |
| ADU 4 | *Continuous precipitation pH 9·2 | | |
| ADU W | *Batch precipitated with $NH_4OH$ solution | Type 1 | Yes |
| ADU Y9 | *Precipitated with $NH_3$ | | |
| ADU Y14 | *Precipitated with $NH_3$ | | |
| ADU C937 | †$NH_3$ passed into uranyl nitrate solution; ppt dried 105°C | | Yes |
| ADU C938 | †Precipitated with $NH_4OH$; dried 105°C | | Yes |
| ADU C939 | †Precipitated as C937; dried in vacuo over $P_2O_5$ | | Yes |
| ADU C940 | †C939 further dried at 105°C | | Yes |

* Supplied by Dr. R. SOWDEN.
† Supplied by Mr. J. WALKDEN
‡ Type 2: X-ray diagram identical to that for the usual form of $UO_3.2H_2O$.

TABLE 2.—CHEMICAL ANALYSIS OF SOME ADU SAMPLES AFTER DRYING AT 105°C

| Sample | Composition (molar) | | | |
|---|---|---|---|---|
| | U | $NH_3$ | $H_2O$* | $NO_3^-$ |
| ADU C | 1 | 0·57 | 1·05 | 0·2 |
| ADU 1 | 1 | 0·27 | 1·50 | 0·1 |
| ADU 2 | 1 | 0·19 | 1·14 | 0·05 |
| ADU W | 1 | 0·56 | 1·25 | 0·1 |
| ADU C937 | 1 | 0·44 | 1·33 | — |
| ADU C938 | 1 | 0·57 | 1·31 | 0·1 |
| ADU C939 | 1 | 0·57 | 1·30 | 0·03 |
| ADU C940 | 1 | 0·57 | 1·27 | 0·01 |

* Hydrogen in the sample not accounted for as $NH_3$ is reported as "$H_2O$" for convenience.

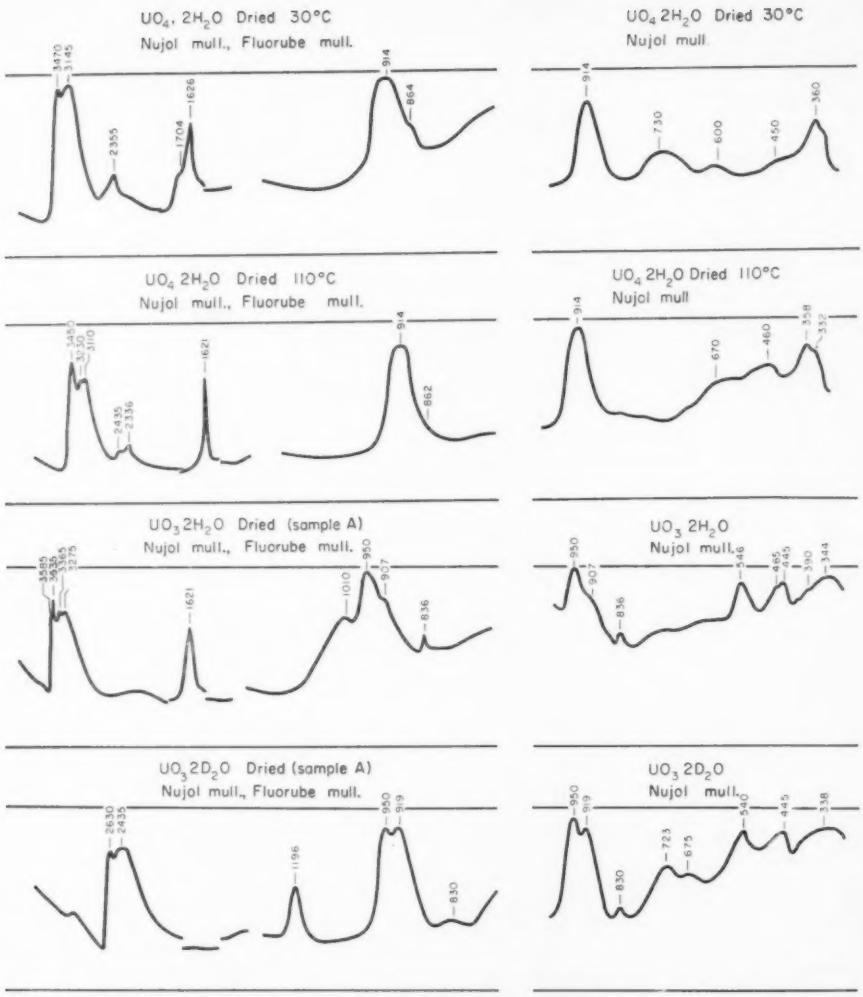


FIG. 1a.—The infra-red spectra of the series of hydrated uranium oxides.

follows: portions were inserted in a cooled combustion tube and the temperature raised to 900°C in a current of oxygen. Copper oxide in the tube was maintained at 900°C by a separate furnace during the run. The water formed was absorbed and weighed to give the total hydrogen in the sample, and the residue in the boat was weighed as $U_3O_8$ to give the uranium content. Ammonia was determined absorptiometrically on further portions using Nessler's reagent after distillation from caustic soda solution. After ammonia had been removed the nitrate in the solution was reduced by Devarda's alloy and the resultant ammonia determined.

X-ray powder patterns were also available on some of the samples indicated in Table 1.

The analysis of these compounds shows that the usual formula written for ADU, viz. $(NH_4)_2U_2O_7$ is completely inadequate to describe it. This point seems to have received surprisingly little attention in the past; it was known that the composition was very variable, and work by ARMSON *et al.*[2] in 1949 showed that the compound is formed with less than the theoretical equivalent of ammonia, but the important part played by water in the composition does not seem to have been emphasized.

[2] F. J. ARMSON, H. E. DIBBEN and H. MASON, SCS-R-30 (declassified 1959).

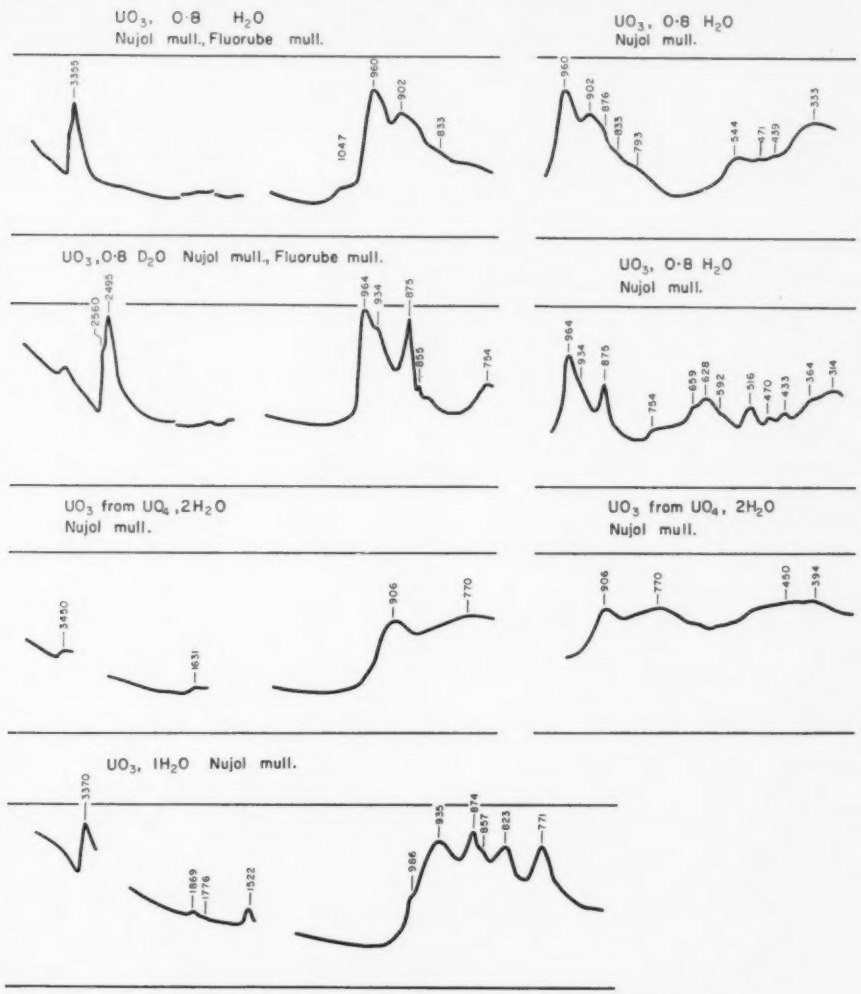


FIG. 1b.—The infra-red spectra of the series of hydrated uranium oxides.

*Spectroscopic technique*

Spectra were obtained using Hilger H800 spectrometer with NaCl and CsBr prisms over the range 5000–300 $cm^{-1}$. Preliminary experiments with $UO_3$ dihydrate showed that the caesium bromide disk technique introduced marked changes in the spectra, especially in the OH bands, spectra of all the compounds were therefore measured in Nujol and fluorube mulls, and in some cases also in an alkali halide disc. A quantitative study of the variation of spectra with particle size was not carried out, but it appears, from the variations which have been observed in replicate spectra using varying grinding conditions, particle size affects the quality of the spectrum. It does not appear that any spurious peaks are introduced, but it is not possible to base quantitative measurements on band areas in the spectra which were obtained. Some spectra were measured with the sample indirectly cooled by liquid oxygen; a spectacular sharpening of some bands resulted, but close study of the room- and low-temperature spectra suggests that the effects are confined to band sharpening and small frequency shifts. Room-temperature measurements can be fitted into the same relationships as the low-temperature measurements.



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## RESULTS

### *The* $UO_3$ *hydrates*

(*a*) *The* 700–1200 *cm*$^{-1}$ region. The spectra of all the hydrated oxides examined (Fig. 1) and also a large number of the ammonium diuranate spectra show a strong band near 900 cm$^{-1}$ which can be assigned to the antisymmetric stretching frequency of the uranyl group (it has been stated[3] that all $UO_3$ samples except the cubic form exhibit uranyl-type bonding in their structure). This region also contains a number of other bands which require assignment. It was recently suggested by GENTILE *et al.*[4] that in the uranium trioxide-water system uranic acid, $UO_2(OH)_2$, is present, and BERGSTROM and LUNDGREN[5] have carried out an X-ray investigation of $\beta$-$UO_3.1H_2O$, on the basis of which they suggest a structure consisting of OUO chains with each U atom surrounded by four OH groups. If any of these compounds do in fact contain —OH groups instead of water molecules in the structure, this should result in OH deformation bands appearing in the 1000–700 cm$^{-1}$ region. The deuteration experiments were undertaken to check this. In the dihydrate two bands at 1010 cm$^{-1}$ and 907 cm$^{-1}$ move to 723 cm$^{-1}$ and 675 cm$^{-1}$ respectively on deuteration and must be assigned as deformation bands, $\delta_{OH}$. In the lower hydrate ($UO_3.0{\cdot}8H_2O$) the group of bands from 793 to 902 cm$^{-1}$ moves to 592 to 754 cm$^{-1}$ in the deuterated compound. These shifts confirm the presence in both compounds of OH groups attached to the uranium atom. The dihydrate also shows a band which shifts from 1621 to 1196 cm$^{-1}$ on deuteration, corresponding to the deformation vibration of the $H_2O$ molecule, and in the dihydrate some of the water must be present in molecular form. In the deuterated forms, the origin of the bands at 919 cm$^{-1}$ in the dihydrate and at 875 cm$^{-1}$ in the lower hydrate is uncertain; unlike the uranyl band, these bands are relatively sharp (intensity markedly dependent on resolution). It is unlikely that they correspond to the symmetric stretch of the uranyl group, as the frequency is too high. (An examination of the Raman spectrum, which would reveal the symmetric uranyl vibration, may assist in this assignment, and we hope to undertake this shortly.) Failure to vary in intensity with isotopic purity rules out their origin in the $\delta_{OH}$ bands of the hydrogen isotope which is present in small quantities in the samples.

(*b*) *The* 3000 cm$^{-1}$ *region.* This region contains the OH stretching vibrations both of the hydroxyl group and of the water molecule. In $UO_3.0{\cdot}8H_2O$ this vibration consists of a single sharp band with a small shoulder on the high-frequency side, yet the deformation vibration is a complex of three components. TARTE[6] has shown that in the basic copper salts a similar phenomenon is observed, and he attributes the excess of deformation frequencies over stretching frequencies to the presence in the molecule of two different Cu–O– distances in the CuOH groups. It is possible that in the $UO_3$ hydrate there may again be different UO distances in the UOH groups: this will have very little effect on the stretching vibrations[6]; however, in the deuterated form the stretching vibrations just splits into three components on cooling (Fig. 4). The instrumental resolution is about 1·8 times better in the region of $\nu_{OD}$ than in the $\nu_{OH}$ region, while the splitting of the $\nu_{OD}$ bands will be $\sqrt{2}$ times less than that of the

[3] H. R. HOEKSTRA, and S. SIEGEL, Second U.N. Conference: A/Conf.16/P/1548.
[4] P. S. GENTILE, L. H. TALLEY T. J. COLLOPY, *J. Inorg. Nucl. Chem.* **10**, 114 (1959).
[5] G. BERGSTROM and G. LUNDGREN *Acta. Chem. Scand.* **10**, 673 (1956).
[6] T. TARTE, *Spectrochim. Acta.* **13**, 107 (1958).

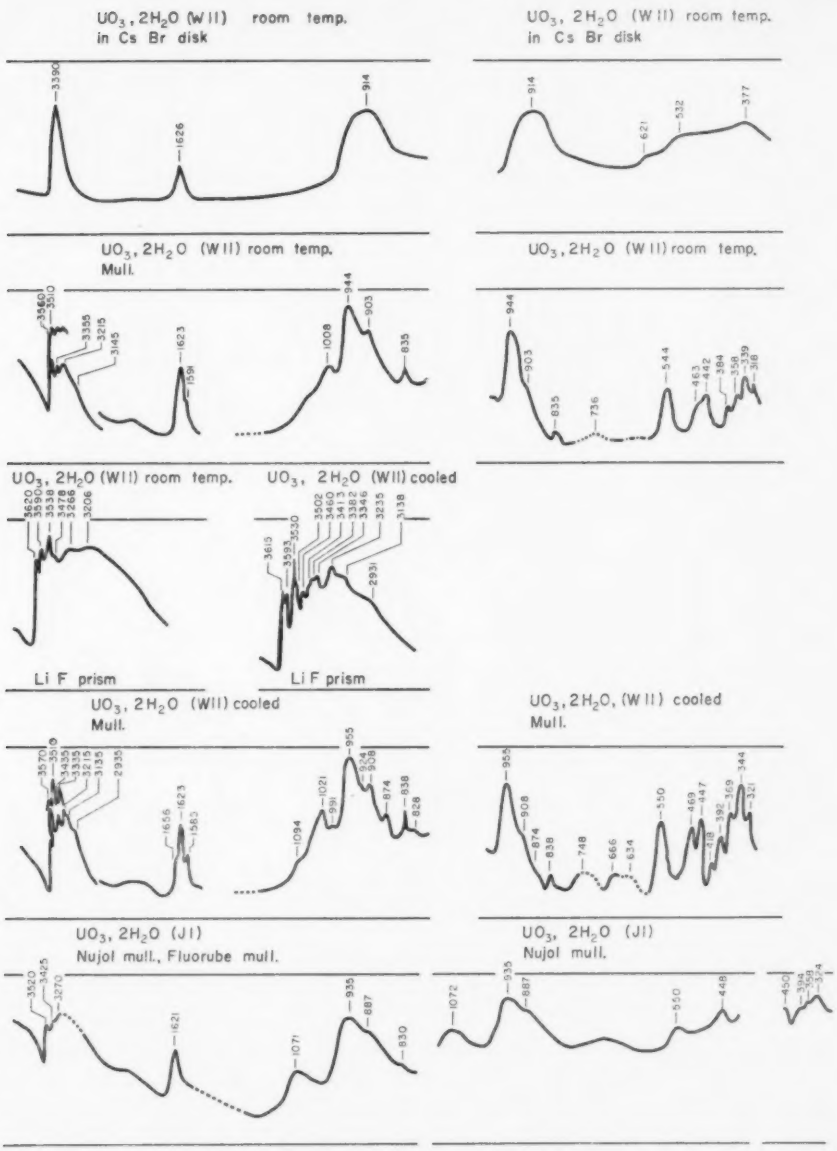


FIG. 2.—Infra-red spectra of the $UO_3$ dihydrate, sample (W 11), under various conditions, and the spectrum of the dihydrate sample (J 1).

$\nu_{OH}$ bands, so that when splitting of the O–D vibrations is just resolved, that of the O–H vibrations will not be detected; it seems probable therefore that the multiple deformation frequencies results from different hydrogen bond strengths.

The spectra in the 3000 $cm^{-1}$ region are much more complex for the dihydrate than for the monohydrate. In one sample in particular (W11) which was a well-defined crystalline material, eleven peaks are observed when the spectrum is sharpened by cooling to liquid oxygen temperature and examined with LiF resolution (Fig. 2).

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This is accompanied by sharpening of the subsidiary bands in the 700–1200 $cm^{-1}$ region, and Fig. 3 shows that a good correlation exists between the frequencies of these two sets of bands. The points on this straight line also lie well within the limits of the correlation plotted by Tarte for the basic copper salts, though with a rather larger slope than he selected. It is more convenient to plot the bands observed with NaCl resolution, as this compares more closely with that observed in other regions of the spectrum: Table 3 shows the correlations plotted. The correlation confirms

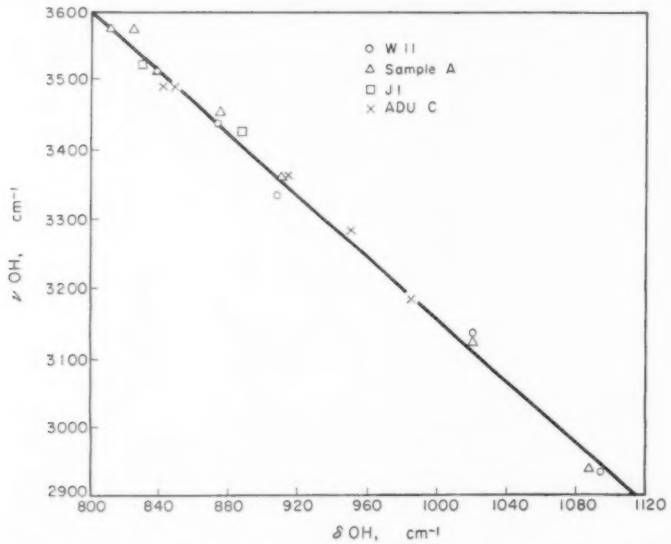


FIG. 3.—Correlation of the $\nu_{OH}$ and $\delta_{OH}$-frequencies of $UO_3.2H_2O$ and ADU C.

that this complex of vibrations arises from different hydrogen-bond strengths in the crystal.

(*c*) 300–700 $cm^{-1}$ *region*. $UO_3.2H_2O$ shows three prominent bands at room temperature which require assignment. The simplest to assign is that at approximately 350 $cm^{-1}$, which shows some structure on its sides. This band is common to all the samples examined, is unchanged on deuteration and would seem to have only three possible origins; it may be due to the uranyl deformation frequency, to the uranium oxygen vibration of a UOH group in the molecule, or to the OH · · · O stretching vibration, which normally occurs in the range 250-100 $cm^{-1}$.[7] This latter vibration is coupled to the $\nu_{OH}$ vibration, and its frequency should be proportional to the width of the $\nu_{OH}$ band. There is clearly no relation between the frequencies observed near 350 $cm^{-1}$ in Fig. 2 and the width of the corresponding $\nu_{OH}$ bands (see below and Table 3), so it appears unlikely that the 350 $cm^{-1}$ group can be assigned to the OH · · · O group. The spectra of the $UO_3.2H_2O$ samples in different preparations offer some guidance in the assignment of the bands to the UO vibration of the UOH group rather than the uranyl deformation. In a caesium bromide disk this band is a single

[7] N. SHEPPARD, "*Hydrogen Bonding*" (Edited by D. Hadzi and H. W. Thompson) p. 85. Pergamon Press, Oxford (1959).

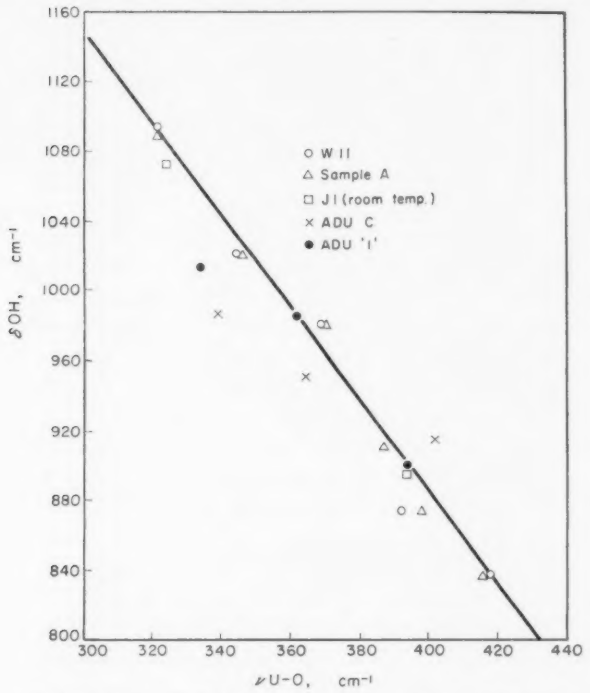


FIG. 4 —Correlation of $\delta_{OH}$ and $\nu_{UO}$ frequencies of $UO_3.2H_2O$ and ADU.

TABLE 3.—THE $\nu_{OH}$, $\delta_{OH}$ AND $\nu_{U-O}$ BANDS OF SOME $UO_3.2H_2O$ SAMPLES AT LIQUID OXYGEN TEMPERATURE

| | $\nu_{OH}$ ($cm^{-1}$) | $\delta_{OH}$ ($cm^{-1}$) | | $\nu_{U-O}$ ($cm^{-1}$) | |
|---|---|---|---|---|---|
| W11 | Sample A | W11 | Sample A | W11 | Sample A |
| 3570 | 3580 | | 811<br>825 | | |
| 3510 | 3510 | 838 | 838 | 418 | 417 |
| 3435 | 3450 | 874 | 875 | 392 | 398 |
| 3335 | 3360 | 908 | 911 | | 387 |
| 3215 | 3225 | Calculated 970 | Calculated 970 | 369 | 370 |
| 3135 | 3125 | 1021 | 1021 | 344 | 346 |
| 2935 | 2940 | 1094 | 1089 | 321 | 321 |

broad band with no observable structure, but in Nujol a number of higher frequency components become apparent, which are greatly sharpened on cooling; these can be correlated (Fig. 4, Table 3) with the fine structure of the OH stretching and deformation frequencies already mentioned for this material (Fig. 3) which also collapse into a single band in a halide disk. Since the band is unchanged on deuteration it cannot be due to any of the hydrogen bond deformations, so the inductive influence of the hydrogen bond through the oxygen atom must be responsible for the splitting, and this vibration must be the UO vibration.

The two other bands in this region at ~550 $cm^{-1}$ and 450 $cm^{-1}$ are still unassigned. The frequency is too high to be due to uranyl deformation, and neither band persists throughout the whole series of compounds examined. In the ammonium diuranates the 550 $cm^{-1}$ band is only vestigial, whereas a 460 $cm^{-1}$ band is quite prominent. In $UO_3.8H_2O$ only the 550 $cm^{-1}$ band can be faintly seen, the 450 $cm^{-1}$ band having almost vanished. It seems difficult to devise a structure which would permit either of these bonds to arise as a –U–O–U–O stretch while retaining the $(UO_2)(OH_2)$ structure, and the most reasonable assignment for these two bands is to suggest that they are both due to a uranium–oxygen link by which the water molecule in the dihydrate structure is co-ordinated to the uranium: this must result in two distinct bond strengths for the latter co-ordination. At low temperatures the 450 $cm^{-1}$ band splits into two components while the 550 $cm^{-1}$ band remains single; the $H_2O$ deformation band is split into three components on cooling, supporting this assignment of the 450 $cm^{-1}$ and 550 $cm^{-1}$ bands. In the deuterated forms the splitting of $\nu_{OD}$, $\delta_{OD}$, $\nu_{UO}$ bands and the 450 $cm^{-1}$ band is less marked, and further confirms the proposed assignments. The multiple bands almost certainly imply that there is more than one U ← O distance in the structure, and this is likely to be related to the multiple hydrogen bond pattern observed.

*Ammomiun diuranate*

The spectra of all the ADU samples are broadly similar, but show detailed differences in all regions of the spectra. The specimen ADU "C" showed a pattern in which much of the structure could be correlated with that observed in samples of $UO_3$ dihydrate, and this specimen has been used as the basis of the proposed structure outlined here.

(*a*) *The spectrum of* ADU "C". Figure 5 shows the spectra at room temperature and at liquid oxygen temperature in a Nujol mull and at liquid oxygen temperature in a potassium bromide disk. Comparison of the spectra with the $UO_3$ dihydrate spectrum shows common features at ~3000, 1000 and 350 $cm^{-1}$. It seems reasonable to assign these features to the same origins as those which have been concluded for the $UO_3$ dihydrate, and this is confirmed by the fit of the points on the same line as that for the $UO_3$ hydrate in Fig. 3 (the band at 914 $cm^{-1}$ is a weak dimple which can be seen in the original spectrum superimposed on the broad uranyl frequency which is present at about the same frequency) and by the fairly good correlation between the $\delta_{OH}$ frequencies and $\nu_{U-O}$ frequencies in Fig. 4, although this relationship is not identical with that observed in the $UO_3$ hydrates. This may be explained in terms of a slightly different UO distance in the ADU structure, but there seems no reason to doubt the assignment of this group of bands to the U–O stretching vibration of the UOH group in the structure. Analysis of the material shows that the molecule

contains approximately one molecule of water and 0·6 molecules of $NH_3$ to one atom of uranium. The intensities of bands which have been assigned to OH stretch and to U–O stretch are comparable with those for similar bands in the $UO_3$ dihydrate, which suggests that virtually all the water present in the ADU "C" sample is in the

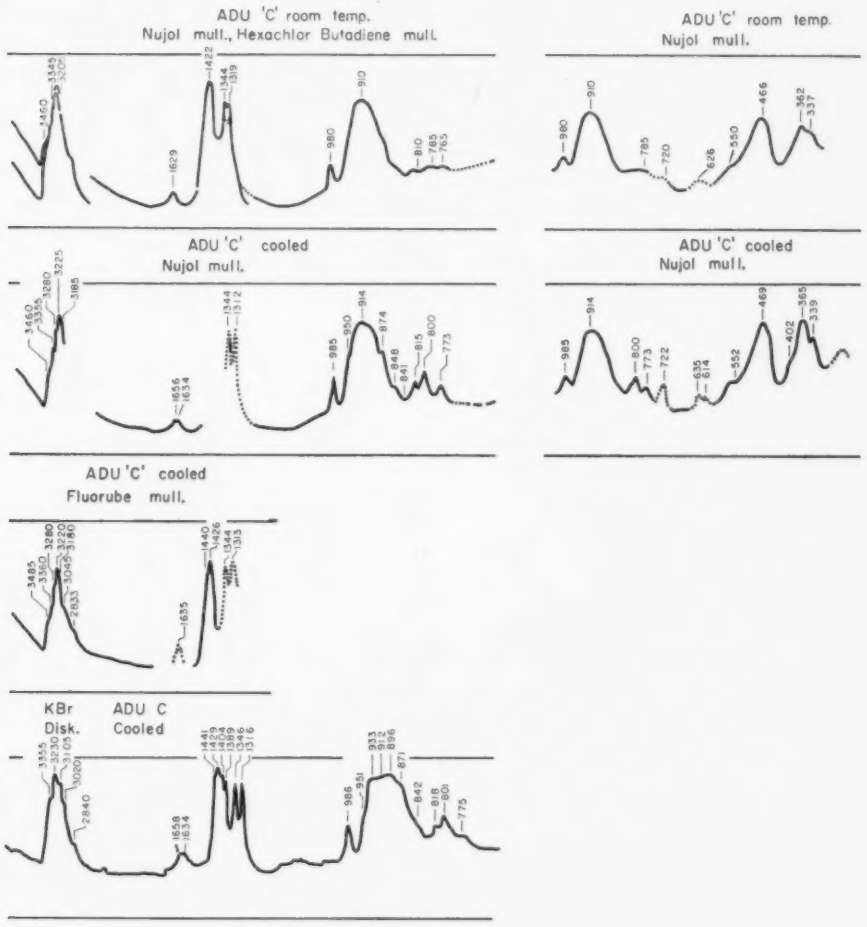


FIG. 5.—Infra-red spectrum of ADU "C".

$U(OH)_2$ form. The strong band at 469 $cm^{-1}$ is shifted slightly from the position at which a band occurs in the $UO_3$ dihydrate spectra assigned to the UO link of a co-ordinated water molecule, and a second weak band at ~550 $cm^{-1}$ occurs in a position which has been similarly assigned. The intensity of the 469 $cm^{-1}$ band seems too great to be accounted for by the amount of water which can be present in molecular form especially if we consider the intensity of the deformation frequency at ~1630 $cm^{-1}$ which might be assigned to deformation of the $H_2O$ molecule. It is tempting to assign the 469 $cm^{-1}$ vibration to the U ← N stretch of an $NH_3$ group co-ordinated to the uranium, since it might reasonably be expected that this would absorb somewhere in

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this region, and there seems to be no mechanism by which $NH_4^+$ ions can be fitted into the $UO_2(OH)_2$ structure.

There is no direct evidence to justify the assignment of the 469 $cm^{-1}$ band to the U ← N stretch; isotopic substitution has not been attempted, but if it were shown that a series of samples could be prepared with this band in a constant position, this would be an interesting experiment. This band moves by several $cm^{-1}$ for the methods of preparation used for the samples studied, and thus the shift to be expected on changing the nitrogen isotope would not be detected. This variation of band position between samples is common to all the main groups of bands in the spectrum.

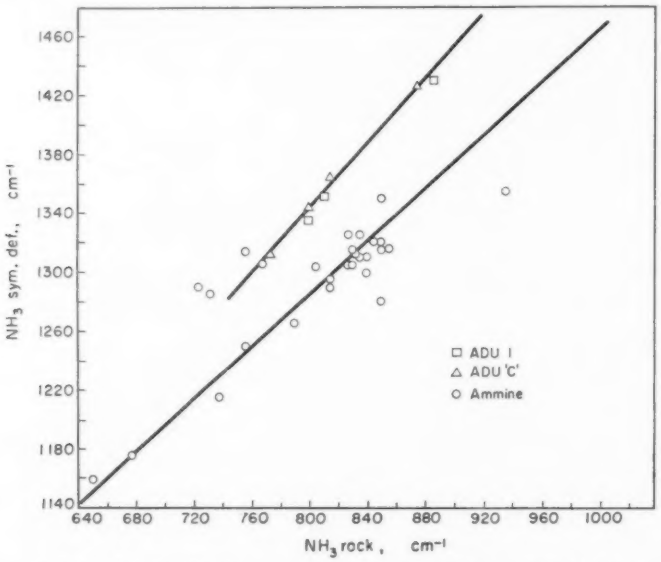


FIG. 6.—Relationship between symmetric deformation and rocking frequencies in ammines (after Svatos) and in ADU.

Having proposed that the structure contains co-ordinated $NH_3$ groups we are now in a position to assign virtually all the remaining bands in the spectrum without requiring the presence of $NH_4^+$ groups. SVATOS[8] has listed the various deformation vibrations which are observed in twenty-eight ammine complexes. Three separate NH deformations, are observed, viz.

(i) a degenerate $NH_3$ deformation between 1650 and 1560 $cm^{-1}$, apparently not influenced by the nature of the metal; the distribution within this range appears to be random.

(ii) An $NH_3$ symmetric deformation frequency in the range 1150 to 1350 $cm^{-1}$, sensitive to the nature of the central atom to which the $NH_3$ is co-ordinated and

(iii) an $NH_3$ rocking vibration between 650 and 950 $cm^{-1}$, which is even more sensitive to change.

In Fig. 6 the symmetric deformation frequencies listed by SVATOS are plotted against the rocking frequencies. There appears to be a rough correlation between

[8] G. SVATOS, D. M. SWEENY, S. MIZUSHIMA, C. CURRAN, J. V. QUAGLIANO, *J. Amer. Chem. Soc.* **79**, 3313 (1956).

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TABLE 4.—OBSERVED BANDS AND ASSIGNMENTS IN ADU "C" AND ADU "1" (COOLED SAMPLES)

| Band ($cm^{-1}$) | | Assignment |
|---|---|---|
| ADU "C" | ADU "1" | |
| | 3549 | $\nu_{OH}$ |
| 3489 | 3470 | $\nu_{OH}$ |
| 3360 | 3400 | $\nu_{OH}$ |
| 3280 | | $\nu_{OH}$ |
| 3220 | 3225 | $\nu_{NH}$ ($+\nu_{OH}$ of ADU 1) |
| 3180 | | $\nu_{OH}$ |
| 3045 | | 1426 + 1634 |
| 2833 | 2840 | $2 \times \delta_{NH}$ ($2 \times 1426$; $2 \times 1429$) |
| 1656 | | $H_2O$ deformation |
| 1634 | | ← $NH_3$ degenerate deformation |
| | 1629 | ← $NH_3$ degenerate deformation |
| | 1603 | and $H_2O$ deformation |
| 1440 | 1443 | |
| 1426 | 1429 | $NH_3$ symmetric deformation |
| | 1408 | |
| 1380 | 1379 | $NO_3^-$ (sharp band at 1388 in KBr disk) |
| 1344 | 1352 | $NH_3$ symmetric deformations |
| 1312 | 1335 | |
| | 1012 | $\delta_{OH}$ |
| 985 | 982 | $\delta_{OH}$ |
| 950 | | $\delta_{OH}$ |
| | 928 | $\nu_a$, antisymmetric stretch of $UO^{2+}$ |
| 914 | | $\nu_a$ of $UO_2^{2+}$ + $\delta_{OH}$ |
| | *(899) | $\delta_{OH}$ |
| | *(886) | ← $NH_3$ rock |
| 874 | | ← $NH_3$ rock |
| 848 | | $\delta_{OH}$ |
| 841 | | $\delta_{OH}$? |
| | 828 | $\delta_{OH}$ |
| 815 | 811 | ← $NH_3$ rock |
| 800 | 800 | ← $NH_3$ rock |
| | 784 | |
| 773 | 765 | ← $NH_3$ rock |
| 552 | 534 | U ← O stretch |
| | 496 | U ← N stretch } tentative |
| 469 | | U ← N stretch } assignment |
| | 451 | U ← O stretch |
| 402 | 394 | |
| 365 | 362 | U—O—stretch |
| 339 | 334 | |

* Bands present only as inflexions on the strong 928 $cm^{-1}$ band.

these; a straight line can be drawn which gives fair agreement with most of the points, although there is considerable scatter.

In the spectrum of ADU "C" we find that there are two bands at ~1630 $cm^{-1}$; one at 1656 $cm^{-1}$ is reduced in intensity on drying at 105°C. It is proposed that the latter is the deformation frequency of the water in the damp ADU. The intensity is

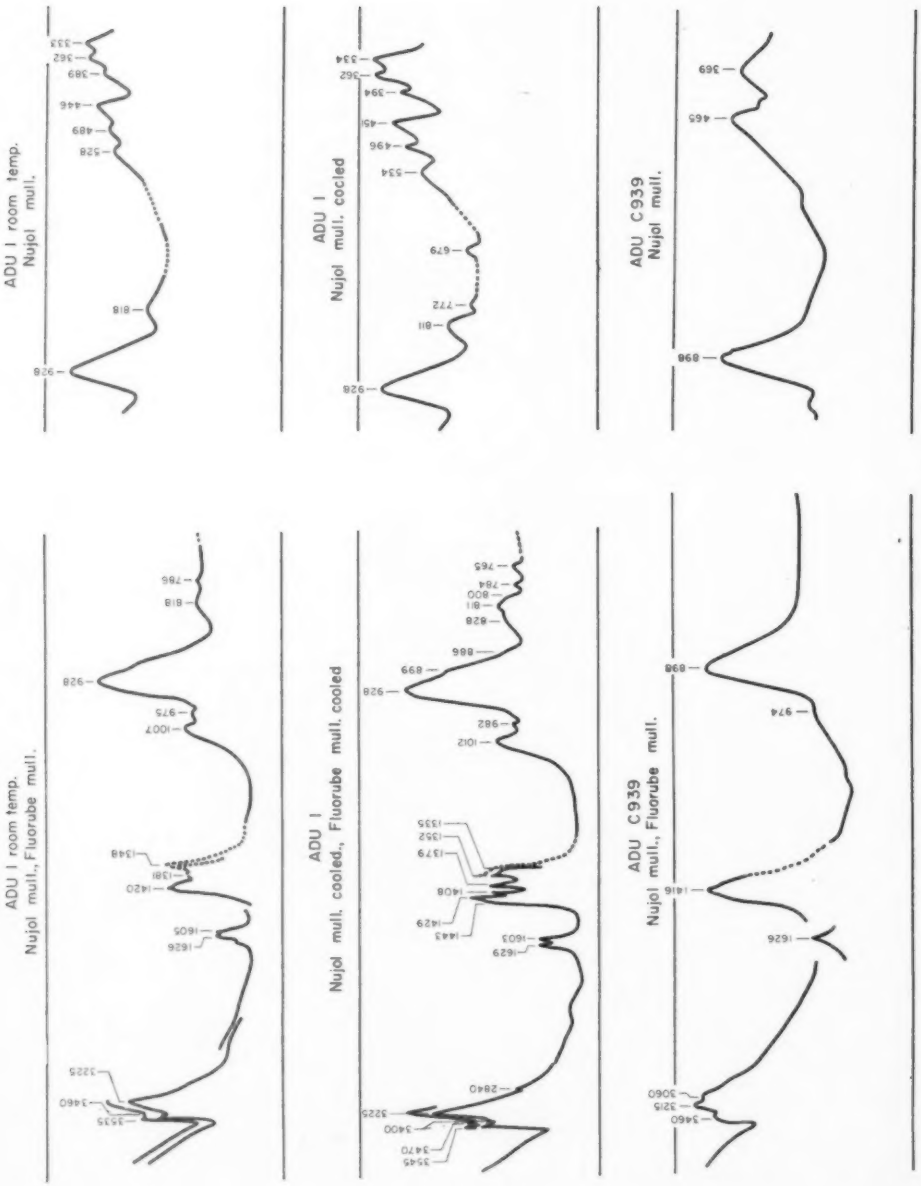


FIG. 7.—The infra-red spectrum of ADU '1' and ADU C939.

small and the amount of water present is obviously not great. The second band at 1634 $cm^{-1}$ is not affected by drying, and it is proposed that this is the degenerate deformation frequency of the $NH_3$ group. Two more groups of bands are unassigned between 1300 and 1450 $cm^{-1}$ and ~800 $cm^{-1}$. There is no doubt that the 1400 $cm^{-1}$ group represent NH deformations, but the 1312 and 1344 bands are rather puzzling, as they are only present in some samples of ADU. However, as can be seen in Fig. 6, there is an excellent linear relationship between the bands in the 800 $cm^{-1}$ region, which have consequently been assigned in Table 4 to $NH_3$ rocking vibrations, and the 1300–1400 $cm^{-1}$ group. The straight lines lies well within the scatter observed by SVATOS for the ammine complexes, and it seems reasonable to assign all these bands to the various $NH_3$ frequencies. (The 1365 $cm^{-1}$ band was only observed in one alkali disk spectrum, with an inflexion on the 1346 $cm^{-1}$ band in another, but this is probably because in both the Nujol and fluorube mulls this region of the spectrum is obscured by bands of the mulling material.) Among the bands tabulated in Table 4 there are now only 2 weak bands unassigned, at 3045 and 2833 $cm^{-1}$. WADDINGTON[9] has proposed that the ammonium ion bands in these positions, assigned respectively as $\nu_2 + \nu_4$ and as $2\nu_4$, indicate that the ammonium ion is locked in position in the lattice and is not free to rotate. It is likely that a similar mechanism operates when these bands are observed in the ← $NH_3$ group, and in fact these bands are weak in all the ammonium diuranates in the Nujol mull, but are strengthened in potassium bromide and very considerably strengthened in caesium bromide disks. This effect is probably analogous to the blurring of the hydrogen bond pattern in the hydrated $UO_3$ samples, and is due to the bonding of the $NH_3$ to the caesium bromide lattice preventing rotation. If this assignment is accepted, it indicates that the ← $NH_3$ groups in the ADU structure are very lightly restrained by hydrogen bond forces and provides a satisfactory assignment of the last unexplained bands in the spectrum of ammonium diuranate as overtone and combination bands of the deformation frequencies.

(*b*) *The spectrum of* ADU "1' Having assigned the bands observed in ADU "C", the assignment can be extended to explain the observed bands in other samples of the product.

Figure 7 shows the spectrum of ADU '1', both at room temperature and when cooled; this spectrum is intermediate between that of ADU "C", and the simpler type which was frequently observed, as instanced by ADU.C939 in the figure. The observed bands are tabulated and assigned in Table 4, and it can be seen that a number of expected bands are now masked by other features of the spectrum, e.g. the $\delta_{OH}$ bands corresponding to the $\nu_{OH}$ bands at 3470 and 3400 $cm^{-1}$ are lost on the side of the strong uranyl deformation band, and the $\nu_{OH}$ bands corresponding to the 1012 and 982 $cm^{-1}$ $\delta_{OH}$ bands are not separated from the NH stretching vibration at 3225 $cm^{-1}$.

This sample contains rather more water than ADU "C", ($1{\cdot}5H_2O/1U$ at 105°C), and it is proposed that the 534 $cm^{-1}$ and 451 $cm^{-1}$ bands are due to U ← O links, and the 496 $cm^{-1}$ band to a U ← N link. The 496 $cm^{-1}$ band was not present in ADU "C"; on the limited evidence of the samples for which the X-ray powder diagram was obtained it seems to characterize those ADU's which have the type "2" powder pattern. This X-ray pattern is identical with that for $UO_3.2H_2O$, but the 496 $cm^{-1}$ band is absent in the latter compound, supporting the assignment at this frequency to the U ← N bond.

[9] T. C. Waddington, *J. Chem. Soc.* 4340 (1958).

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(*c*) *The spectra of other* ADU *samples.* The general features of other ADU, samples resembling C939 in Fig. 7 are similar to those of ADU "C", but the multiplicity of bands is not present; the individual types of vibrations are generally represented by only one band, and the region ~900 $cm^{-1}$ should contain unresolved bands under the uranyl band.

In studying these spectra there seems no reason to think that any other structure is necessary to explain features of the observed bands. For example, there is no evidence that the ammonium ion is present in the structures.

Slight confirmation of this is offered by the spectrum of sodium diuranate; only one sample of this has been examined, which contained at least two components having different crystal colours, but the complete absence of any band in the region 300–420 $cm^{-1}$ in which the UOH assignment has been proposed would be consistent with the structure in which the sodium salt of the uranic acid was formed, $UO^- Na^+$. It seems reasonable that this might raise the frequency of the UO vibration and in fact it is possible that it is found at a wavelength slightly above 420 $cm^{-1}$ in the sodium diuranate sample, but this has not been fully investigated.

Chemical analysis of a number of the ADU samples shows that in none of them is there more than about 0·6 mole of $NH_3$ per mole of uranium, accompanied by about 1·3 mole of water in the highest cases. It seems probable that the equilibrium structure is $UO_2(OH)_2.xNH_3.yH_2O$.

## DISCUSSION

The spectra of the $UO_3$ hydrates examined are consistent with a structure based on uranyl groups with approximately two (OH) groups attached to each uranium atom; in the dihydrate one water molecule is present for each uranium atom. There are apparently two U ← O bond lengths in the lattice of the dihydrate and an exceptionally complex hydrogen bond pattern. Some empirical relationships between the —OH stretching and deformation frequencies and the U–O frequencies are shown. The $UO_3 1{\cdot}OH_2O$ spectrum has been included in the series for completeness but has not yet been examined in detail; it is likely that this compound has a rather different structure. Hydrates derived from other polymorphic forms of $UO_3$ also have a different structure, and it is hoped to consider these in a later paper.

The infra-red spectrum of one sample of ammonium diuranate has been analysed in detail and it has been shown that the structure approximates the form $UO_2(OH)_2$-$NH_3$, with some deficiency of $NH_3$. Unfortunately this sample, which proved most amenable to analysis, was one held in the laboratory about which no preparative information was available. The spectra of a number of other ammonium diuranates which have been examined are broadly similar, though they differ in detail in all regions of the spectrum; in some cases, e.g. ADU "1", the spectrum is still suitable for detailed analysis. It is probable that the structure of these is basically the same as that of the sample which was studied in detail, except that there is rather more water in those molecules than in ADU "C", which showed an overall deficiency; the structure usually approximates to $[UO_2(OH)_2NH_3]_2UO_2(OH)_2H_2O$.

*Acknowledgements*—I should like to thank Dr. E. WAIT and A. C. FOX, who supplied some of the samples and obtained the x-ray diagrams, Mr. J. WALKDEN, who undertook the chemical analysis and supplied other samples, Dr. R. G. SOWDEN, who suggested this work and supplied many of the samples, and Drs. L. F. BOVEY, E. W. RICHARDS and other members of the Spectroscopy Group for helpful discussions.

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# THE PREPARATION AND STRUCTURE OF $K_2NaCrF_6$, $K_2NaFeF_6$ AND $K_2NaGaF_6$

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**Abstract**—Compounds in the elpasolite, $K_2NaAlF_6$, series have been synthesized with Cr, Fe and Ga substituted for Al. The preparations were done by high-temperature non-aqueous methods, in which the metal trifluoride was reacted with potassium and sodium bifluorides. By optical and X-ray analysis they have been shown to belong to space group $O_h^5$-*Fm3m* with lattice constants of 8·266, 8·323 and 8·246 Å respectively. Least squares refinement of the powder data gives for the regular octahedra of fluorides around the transition metal ion distances of 1·933 ± 0·011 for Cr–F and 1·910 ± 0·006 Å for Fe–F. The effect of the structure on the anisotropic temperature factors is discussed.

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IN the search for a fluoride in which a $3d^3$ ion is surrounded by a perfect octahedron of F, to be used in NMR studies with SHULMAN,[1] the elpasolite, $K_2NaAlF_6$, structure series has been investigated with various $Me^{3+}$ ions substituted for the Al. Although the prototype aluminium compound has been assigned[2,3] to space group $T_h^6$-*Pa3* in which the fluoride octahedra around the Al have a trigonal distortion, the evidence is not definitive. Indeed, BRIGHT and WURM[4] found no reflections other than those with all even or all odd indices for powdered $K_2NaTiF_6$, and HELMHOLZ[5] reported that he could not detect any deviations from space group $O_h^5$-*Fm3m* in $K_2NaAlF_6$ nor $K_2NaGaF_6$. We have made $K_2NaCrF_6$ for which X-ray investigation of both powders and single crystals show the most probable space group to be $O_h^5$-*Fm3m*. The iron (III) and gallium compounds have also been made, and the structure of the former determined.

## EXPERIMENTAL

*Preparation.* Fluorides prepared from aqueous solution are seldom pure, as shown for example by BROSSET,[6] and so, although elpasolite can be precipitated from water solutions, we investigated preparations by high-temperature non-aqueous methods. The three compounds $K_2NaCrF_6$, $K_2NaFeF_6$ and $K_2NaGaF_6$ were prepared by adding with stirring the trivalent fluorides to a mixture of $2KHF_2 + 1NaHF_2$ fused in platinum crucible over an open flame. The starting trifluorides were prepared as follows:

(1) $CrF_3$ by treating reagent $CrCl_3$ in a platinum boat with anhydrous HF at 850° in a nickel tube;
(2) $FeF_3$ obtained from General Chemical Division of Allied Chemical and Dye Corp.* made by fluorination of $FeCl_3$;
(3) $GaF_3$ by treatment of reagent $GaF_3 \cdot 3H_2O$ as above for $CrCl_3$ with anhydrous HF at 550°C.

The trifluoride was added to the melt until an appreciable solid phase appeared—generally about one-fifth of the stoicheiometric amount. Then the covered crucible was heated for 15 min further.

* We would like to thank Dr. R. MASON for supplying the $FeF_3$.

[1] R. G. SHULMAN and K. KNOX, *Phys. Rev. Lett.* **4**, 603 (1960).
[2] G. MENZER, *Fortschr. Min.* **17**, 61 (1932).
[3] C. FRONDEL, *Amer. Min.* **33**, 84 (1948).
[4] N. F. H. BRIGHT and J. G. WURM, *Canad. J. Chem.* **36**, 615 (1958).
[5] L. HELMHOLZ, *J. Chem. Phys.* **31**, 172 (1959).
[6] C. BROSSET, *Ark. Kemi. Min. Geol.* **21** A, No. 9 (1945).

The cooled melt was leached with water and ethyl alcohol, and the product dried in air at 110°. Typically in a 100 ml. crucible 75 g of bifluorides were used and 80–90 per cent yields obtained.

A second method was also tried on $K_2NaCrF_6$; it consisted of heating the bifluorides with the trifluoride to 500°C in a platinum-lined autoclave, as described by GUGGENHEIM.[7] Up to the stoicheiometric amount of trifluoride can be processed this way, and the product is more crystalline, of sizes up to a few tenths of a millimetre, which could be used for single crystal X-ray analyses. This method could also be of value if the product is extremely sensitive to atmospheric oxidation in the fusion mixture and if compounds containing the volatile $NH_4F$ were to be prepared.

The compounds were identified by their X-ray patterns (see below) and for chromium and iron by analysis for the heavy metal: results; Cr 19·5% (calc. 19·5), Fe 20·1% (calc. 20·6).

Single crystals of these compounds have been grown by melting and slow cooling in a temperature gradient in a sealed pointed platinum crucible, as described by GUGGENHEIM.[7] They melt between 1000° and 1200°, determined by heating to these two temperatures and observing the product. The chromium compound is emerald green, the iron light yellow-brown almost colourless (although when kept at high temperature for several days it turns brown presumably because of loss of fluorine and the formation of some iron (II)), and the gallium colourless.

*X-ray investigation.* Debye-Scherrer photographs of these three compounds show only lines which can be indexed on a face-centred cubic unit cell with lattice constants given in Table 1. The values of HELMHOLZ[5] are given for comparison; the different methods of preparation may account for the difference in lattice constants.

TABLE 1.—LATTICE CONSTANTS

| Compound | This work | HELMHOLZ[5] |
|---|---|---|
| $K_2NaCrF_6$ | 8·266 ± 0·003 | — |
| $K_2NaFe_6$ | 8·323 ± 0·003 | 8·30 |
| $K_2NaGaF_6$ | 8·246 ± 0·003 | 8·20 |

These results are confirmed by investigation of single crystals. All three compounds are optically isotropic, and hence definitely cubic. Precession and rotation photographs of a small irregular single crystal of the Cr compound confirmed that the most probable space group is $O_h^5$-*Fm*3*m*. Long time exposures showed no mixed index reflexions of the type 320 given by FRONDEL[3] for elpasolite and only the systematic absences of the face-centred lattice. The unit cell, then, contains four formula units with the ions in the following positions:

face centring plus

8K in (c) $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{3}{4}\frac{3}{4}\frac{3}{4}$

4Na in (b) $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

4Cr or Fe in (a) 000

24F in (e) ± x00 ⌢

In view of the simplicity of the structure, with only one co-ordinate parameter to be determined, it was refined from powder, rather than single-crystal data since the current interest is in the structure and not the absolute electron density. The intensities were measured on a GE diffractometer using Cu$K_\alpha$ radiation. Comparison of these intensities with those of the Debye-Scherrer and precession photographs showed preferred orientation to be negligible. After the Cr compound had been measured and the calculation completed, a GE reverter became available and was used on the Fe compound. Considerable improvement in signal-to-noise ratio was obtained, and the latter intensities are more accurate.

*Refinement of the structure.* From the observed intensities the $|F_{hkl}|^2$ were derived and fitted to calculated values using the BUSING-LEVY[8] least squares program. Unobserved reflexions were put in as $\frac{1}{2}$ of the estimated minimum observable value with standard deviations of $\frac{1}{2}$ of their own value. Where observed reflexions were due to more than one *hkl* the value attributable to each was assigned

[7] H. GUGGENHEIM, *J. Phys. Chem.* **64**, 938 (1960).
[8] W. R. BUSING and H. A. LEVY, ORNL Central Files Memorandum 59-4-37 (1959).

on the basis of visual estimates of their ratios on the precession photographs. For these reflexions the standard deviations were increased 50 per cent over that calculated by the method used for non-overlapping reflexions where the standard deviation of a count was taken as the square root of the count. The final analysis showed that these assumptions were not wrong. The scattering factors used were those of FREEMAN[9] for $K^+$, $Na^+$ and $F^-$ and those of THOMAS and UMEDA[10] (extrapolated for Cr) with the real part of the dispersion corrections of DAUBEN and TEMPLETON[11] for $Cr^{3+}$ and $Fe^{3+}$.

With individual isotropic temperature factors ($B$) for the ions, the calculation converged rapidly for the fifty-two data of both structures and the six adjustable parameters. Refinement with anisotropic temperature factors ($\beta$) introduces only two more parameters, so as a trial it was carried out, again giving rapid convergence. The resulting parameter values with their standard deviations are given in Table 2, and the calculated and observed intensities (as is usual, not the $|F|^2$ which were refined) using the anisotropic temperature factors in Table 3.

TABLE 2.—STRUCTURAL PARAMETERS

| | $K_2NaCrF_6$ | $K_2NaFeF_6$ |
|---|---|---|
| Isotropic temperature factors | | |
| Weighted $R$* | 13·4(%) | 5·9(%) |
| $B_K$ | 1·46 ± 0·18 | 1·69 ± 0·16 |
| $B_{Na}$ | 1·45 ± 0·44 | 1·15 ± 0·40 |
| $B_{Cr}$ | 0·91 ± 0·15 | 1·01 ± 0·16 |
| $B_F$ | 1·95 ± 0·27 | 1·84 ± 0·19 |
| $x_F$ | 0·2342 ± 0·0015 | 0·2299 ± 0·0008 |
| Anisotropic temperature factors | | |
| Weighted $R$* | 12·4% | 4·6% |
| $\beta_{11K}$ | 0·0053 ± 0·0010 | 0·0063 ± 0·0008 |
| $\beta_{12K}$ | 0·0005 ± 0·0084 | 0·0011 ± 0·0102 |
| $\beta_{11Na}$ | 0·0048 ± 0·0017 | 0·0037 ± 0·0012 |
| $\beta_{11Cr}$ | 0·0038 ± 0·0006 | 0·0042 ± 0·0005 |
| $\beta_{11F}$ | 0·0018 ± 0·0019 | 0·0006 ± 0·0012 |
| $\beta_{22F}$ | 0·0102 ± 0·0015 | 0·0098 ± 0·0009 |
| $x_F$ | 0·2338 ± 0·0013 | 0·2295 ± 0·0007 |

* Based on $|F|^2$ without multiplicity.

It is interesting to observe that although the fit is appreciably better for the Fe compound, the stardard deviations of the parameters are only slightly better. Introduction of the anisotropic temperature factors makes no significant difference in the fluorine $x$-parameter.

## DISCUSSION

The structure of $K_2NaCrF_6$ is shown in Fig. 1; the iron compound has $Fe^{3+}$ substituted in the Cr position. Each transition-metal ion is surrounded by a perfectly regular octahedron of $F^-$ with distances Cr-F = 1·933 ± 0·011 Å and Fe-F = 1·910 ± 0·006 Å. Although statistically the difference between the Cr-F and Fe-F distances is only of possible significance,[12] the order of the size of these distances is the reverse of that expected from theoretical and experimental studies of ionic radii,[13,14] which

[9] A. J. FREEMAN, *Acta Cryst.* **12**, 261 (1959).
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[14] S. GELLER, *Acta Cryst.* **10**, 248 (1957).

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TABLE 3.—X-RAY INTENSITIES ($\times 10^{-4}$), $CuK_\alpha$ RADIATION*

| | $K_2NaCrF_6$ | | $K_2NaFeF_6$ | |
|---|---|---|---|---|
| *hkl* | $I_{obs}$ | $I_{calc}$ | $I_{obs}$ | $I_{calc}$ |
| 111 | 221 | 238 | 308 | 306 |
| 200 | 82 | 93 | 113 | 109 |
| 220 | 814 | 828 | 830 | 850 |
| 311 | 32 | 43 | 47 | 43 |
| 222 | 277 | 295 | 270 | 277 |
| 400 | 750 | 697 | 674 | 634 |
| 331 | 3† | 4 | 6 | 1 |
| 420 | 29 | 34 | 31 | 39 |
| 422 | 285 | 286 | 274 | 278 |
| 511 | 55 | 45 | 61 | 56 |
| 333 | 3† | 0·0 | 1† | 0·2 |
| 440 | 313 | 300 | 283 | 293 |
| 531 | 30 | 30 | 35 | 33 |
| 600 | 2 | 2 | 2 | 3 |
| 442 | 8 | 9 | 7 | 10 |
| 620 | 117 | 97 | 102 | 98 |
| 533 | 8 | 5 | 3 | 5 |
| 622 | 31 | 27 | 19 | 22 |
| 444 | 80 | 74 | 69 | 70 |
| 711 | 4† | 1 | 1† | 0·3 |
| 551 | 21 | 15 | 13 | 19 |
| 640 | 7 | 2 | 5 | 4 |
| 642 | 122 | 107 | 102 | 101 |
| 731 | 4† | 0·5 | 1† | 0·0 |
| 553 | 15 | 9 | 5 | 9 |
| 800 | 34 | 30 | 27 | 27 |
| 733 | 4† | 0·0 | 1† | 0·2 |
| 820 | 4† | 2 | 2 | 2 |
| 644 | 4† | 1 | 2 | 2 |
| 660 | 19 | 19 | 19 | 18 |
| 822 | 38 | 41 | 38 | 34 |
| 751 | 4† | 4 | 1† | 3 |
| 555 | 5 | 3 | 6 | 4 |
| 662 | 8 | 7 | 3 | 5 |
| 840 | 68 | 89 | 81 | 79 |
| 911 | 10 | 9 | 8 | 10 |
| 753 | 5† | 3 | 2 | 1 |
| 842 | 5† | 2 | 1† | 2 |
| 664 | 45 | 37 | 41 | 33 |
| 931 | 24 | 15 | 17 | 15 |
| 844 | 96 | 90 | 67 | 77 |
| 771 | 5† | 0·3 | 1† | 0·0 |
| 933 | 6 | 6 | 5 | 6 |
| 755 | 4 | 4 | 3 | 3 |
| 10,0,0 | 5† | 0·1 | 1† | 0·5 |
| 860 | 5† | 1 | 1† | 1 |
| 10,2,0 | 34 | 48 | 39 | 44 |
| 862 | 91 | 103 | 104 | 81 |
| 951 | 23 | 32 | 23 | 32 |
| 773 | 5† | 0·2 | 1† | 0·2 |
| 10,2,2 | 5† | 6 | 1† | 3 |
| 666 | 5† | 2 | 1† | 1 |

* Individual values for overlapped reflections in brackets estimated from precession photographs; see text.

† Not observed, tabulated value ½ estimated minimum observable.

show $Fe^{3+}$ to be larger than $Cr^{3+}$, and the reversal of order is significant. It must be that other unknown factors are affecting the structures to bring about this change. The sodium ions also have octahedral $F^-$ environments with Na-F = 2·200 ± 0·011 and 2·252 ± 0·006 Å respectively for the Cr and Fe compounds, while the potassium ions have twelve equidistant fluoride ions with $T_d$ symmetry at distances of 2·926 ± 0·002 and 2·948 ± 0·001 respectively.

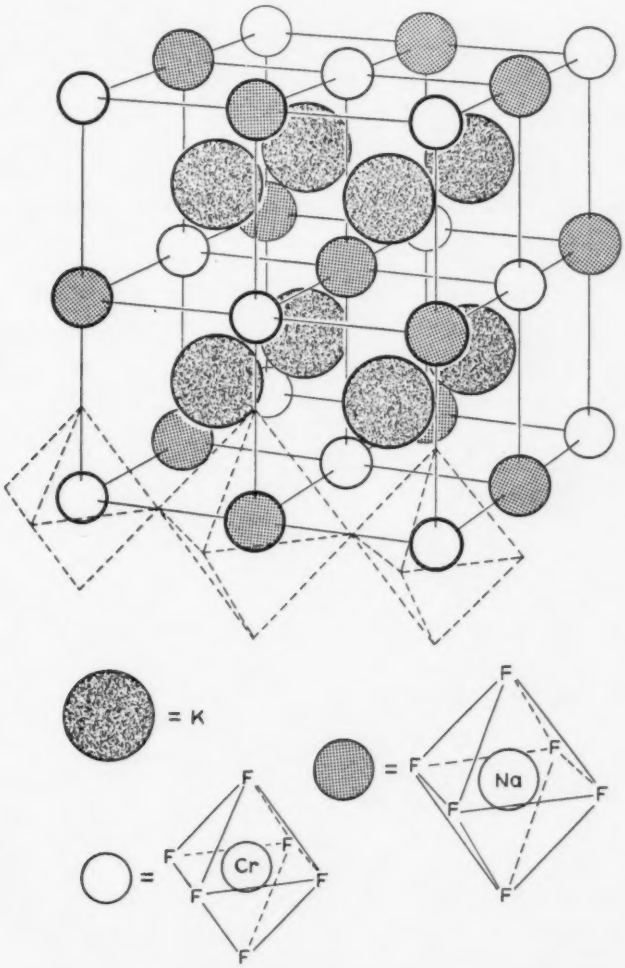


FIG. 1.—Structure of $K_2NaCrF_6$ (only three of the fluorine octahedra are shown).

The potassium and fluoride ions are in an essentially cubic-close-packed array with the smaller chromium or iron and sodium ions in octahedral holes, an arrangement related to that of perovskites. In fact, this structure can be derived from that of a perovskite, say $KMnF_3$, by doubling the perovskite cell in all three dimensions and substituting $Cr^{3+}$ or $Fe^{3+}$ and $Na^+$ ions alternately for the $Mn^{2+}$, the fluoride then no longer being constrained to be equidistant from the $2Mn^{2+}$ but allowed to move

along the line joining $Cr^{3+}$ or $Fe^{3+}$ to $Na^{+}$. As expected, the $F^{-}$ move closer to the smaller $Cr^{3+}$ or $Fe^{3+}$ away from the larger $Na^{+}$. In addition to the twelve near neighbours of the close packing (4K and 8F) the fluoride ion has the Cr or Fe and Na ions as nearest neighbours. The effect of these two nearest metal ions is tentatively indicated by the anisotropic temperature factors, where $\beta_{11}$ representing the amplitude of vibration along the Cr- or Fe-Na direction is very small while $\beta_{22}$ for the vibration perpendicular to this direction is large. In a much less definite way the environment of the $K^{+}$ is reflected in its anisotropic temperature factors. The fluorine $x$-parameter is close to $\frac{1}{4}$; if it were exactly that value, the twelve nearest fluorine neighbours of the $K^{+}$ would be in $O_h$ symmetry not $T_d$, which latter symmetry would only be shown by the next nearest Cr or Fe and Na. Thus, in this situation it is expected that the tetrahedral component of the vibration, $\beta_{12}$, be small while $\beta_{11}$ will have a more usual value. This is in fact the case, but the large standard deviation on $\beta_{12}$ shows that it has not been determined with accuracy and opens any conclusions based on it to some doubt.

We are currently attempting to substitute other trivalent ions, especially heavier transition elements, for the Cr. Early indications show that we have succeeded for $Mo^{3+}$.

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# THE SCANDIUM CHLORIDE–CESIUM CHLORIDE PHASE DIAGRAM*

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THE phase diagram of the scandium chloride–cesium chloride binary system has been investigated by differential thermal analysis. This system contains a congruent melting 3:1 compound $Cs_3ScCl_6$ (m.p. 814°C) and a 3:2 compound $Cs_3Sc_2Cl_9$ with a peritectic point at 619°C (Fig. 1). Two eutectic points are found at 613°C and 569°C corresponding to compositions of 6·5 and 56·5 mole% $ScCl_3$ respectively. No other phase transitions except that of CsCl have been observed.

MEYER[1] studied the formation of double chlorides of $Sc^{3+}$ with NaCl, KCl, RbCl, CsCl and $NH_4Cl$ in aqueous media. He observed double chloride formation only with CsCl, but failed to characterize the compounds.

The two compounds found in the present investigation indicate the existence of octahedral chloro-complexes of scandium. In this regard, as is to be expected, $Sc^{3+}$ is similar to the transition metal ions $Ti^{3+}$, $V^{3+}$ and $Cr^{3+}$. Compounds of the type $A_3MCl_6$ and $A_3M_2Cl_9$ where A is an alkali metal and M is Ti, V or Cr have been characterized in the literature.[2–7]

In particular the crystal structures of the compounds $Cs_3Ti_2Cl_9$, $Cs_3V_2Cl_9$ and $Cs_3Cr_2Cl_9$ have been determined by WESSEL and IJDO.[6] The new compound $Cs_3Sc_2Cl_9$ is presumably isomorphous. In these compounds, two chlorine octahedra share a common face while an $M^{3+}$ ion is situated at the centre of each octahedron.

Anhydrous scandium chloride was prepared by chlorination of the oxide with chlorine and graphite according to the method of PETRŮ.[8] Cesium chloride was dried by melting. The cesium–scandium chloride melts were prepared and handled in silica tubes under an inert atmosphere of dry argon. The clear melts did not wet the silica surface unless subjected to prolonged heating. Previous work[9] has shown wetting to be due to traces of hydroxide and reaction of the melt with the silica. A thermocouple in a thin walled silica container was placed in the melt.

A second silica tube was filled with dry zirconia and also contained a thermocouple. Both silica tubes were inserted in a massive nickel block surrounded by a tubular furnace. The differential thermocouple voltage was registered on an electronic

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.
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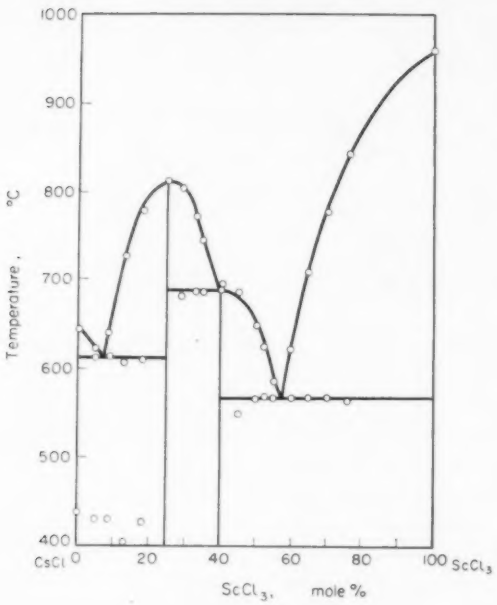


FIG. 1.

TABLE 1.

| Mole % $ScCl_3$ | Observed temperatures* | | | |
|---|---|---|---|---|
| | *a* | *b* | *c* | *b* |
| 75·8 | 842 | 565 | | |
| 69·9 | 777 | 567 | | |
| 64·7 | 707 | 567 | | |
| 59·7 | 622 | 567 | | |
| 55·0 | 588 | 568 | | |
| 52·4 | 624 | 569 | | |
| 49·9 | 648 | 567 | | |
| 44·8 | 684 | 548 | | |
| 40·0 | 691 | | | |
| 35·2 | 743 | | | 684 |
| 33·3 | 772 | | | 685 |
| 28·9 | 811 | | | 681 |
| 25·0 | 814 | | | |
| 18·3 | 778 | 610 | 426 | |
| 13·0 | 728 | 606 | 403 | |
| 8·6 | 641 | 611 | 430 | |
| 4·7 | 622 | 613 | 429 | |
| 0 | 643 | | 436 | |

* *a* = Temperatures of the liquidus line.
*b* = Temperatures of the eutectic points.
*c* = Temperatures of the phase transition of CsCl.
*d* = Temperatures of the peritectic transformation.

recorder during the cooling of the salt melt and the temperature of the cell containing the salt was measured manually at short intervals using a Rubicon Type 2700 Potentiometer. The cooling rate was held at 5°C/min. To reduce errors due to vaporization of scandium chloride the largest mole fraction used was 75 mole % $ScCl_3$. The melting point of the pure compound was taken as 960°C, as reported by FISCHER *et al.*[10] Fig. 1 shows the phase diagram constructed from the data in Table 1.

[10] W. FISCHER, R. GEWEHR, H. WINGCHEN, *Z. Anorg. Chem.* **242,** 161 (1939).

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# THE SYNTHESIS OF POTASSIUM HEXACYANOCHROMATE (O)

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(*Received* 7 *April* 1961)

**Abstract**—The reduction of $K_3Cr(CN)_6$ by potassium in liquid ammonia results in the formation of a green precipitate possessing the empirical formula $K_6Cr(CN)_6$. The properties of the precipitate, as determined by four independent methods—reacting ratio studies, chemical analysis, reducing power determinations, and magnetic measurements—show it to contain chromium in the zero oxidation state.

THE recent work of HIEBER *et al.*[1] and of BEHRENS and KÖHLER[2,3] has shown that cyanyl-carbonyl derivatives of chromium with the general formula $M_xCr(CN)_x(CO)_y$, where $x = 1$, 2, or 3, $x + y = 6$ and M is either Na or K, can be prepared. However, the carbonyl-free cyanide of chromium in the zero oxidation state comparable to $K_4Ni(CN)_4$[4] and $K_8Co_2(CN)_8$[5,6] is, as yet, unreported. Recent studies in these laboratories have shown that a compound having the empirical formula $K_6Cr(CN)_6$ can be prepared by reducing potassium hexacyanochromate (III)[7] with potassium in liquid ammonia. The properties of the product as determined by four different methods—reacting ratio studies, chemical analysis, reducing power determinations, and qualitative magnetic measurements—show it to contain chromium in the zero oxidation state.

The apparatus used in the reduction step was identical to that employed by KLEINBERG and co-workers[8] in a similar study involving the complex cyanides of manganese in the uni- and zero-valence states. The all-glass system was thoroughly dried at 110°C and, after cooling and assembling, was purged with argon to ensure a non-oxidizing atmosphere. Two-hundredths mole (6·4 g) of potassium hexacyanochromate (III), $K_3Cr(CN)_6$, was added to 500 ml of anhydrous liquid ammonia by means of a loading gun. When solution was nearly complete, 0·08 mole (3·1 g) of potassium metal was added by means of a second loading gun. A dark green precipitate formed immediately after the potassium addition. It was found that the deep blue colour characteristic of potassium dissolved in liquid ammonia would persist for more than a few minutes only when the molar reacting ratio of K to $K_3Cr(CN)_6$

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[1] W. HIEBER, W. ABECK and H. PLATLER, *Z. Anorg. Chem.* **280**, 252 (1955).
[2] H. BEHRENS and J. KÖHLER, *Z. Naturforsch.* **14** B, 463 (1959).
[3] H. BEHRENS and J. KÖHLER, *Z. Anorg. Chem.* **306**, 94 (1960).
[4] J. W. EASTES and W. M. BURGESS, *J. Amer. Chem. Soc.* **64**, 1187 (1942).
[5] W. HIEBER and C. BARTENSTEIN, *Naturwissenschaften* **13**, 300 (1952).
[6] G. W. WATT, J. L. HALL, G. R. CHOPPIN and P. S. GENTILE, *J. Amer. Chem.* Soc. **76**, 373 (1954).
[7] J. H. BIGELOW and J. C. BAILAR, *Inorg. Syn.* **2**, 203 (1946).
[8] V. H. CHRISTENSEN, J. KLEINBERG and A. W. DAVIDSON, *J. Amer. Chem. Soc.* **75**, 2495 (1953).

was greater than 3 to 1. This observation strongly suggests that the stoicheiometry of the reaction is that given by the equation:

$$K_3Cr(CN)_6 + 3K \rightarrow K_6Cr(CN)_6 \downarrow \quad (1)$$

The liquid ammonia was removed by vacuum filtration, and the precipitate was washed with five 100 ml portions of liquid ammonia.

The green reaction product was found to be both oxidatively and hydrolytically unstable when exposed to air and was, therefore, handled in an inert atmosphere at all times. A complete analysis of the product gave a K:Cr:CN:$NH_3$ mole ratio of 6·15:1·00:6·15:0·13. These results are the mean of three determinations and suggest an empirical formula of $K_6Cr(CN)_6 \cdot 0{\cdot}1NH_3$. *Anal.* Found: K, 52·83; Cr, 11·36; CN, 35·15; $NH_3$, 0·43. Calc. for $K_6Cr(CN)_6$: K, 52·99; Cr, 11·75; CN, 35·26; $NH_3$, 0·00%.

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The reducing power of the product as determined by reaction with water is in complete accord with the analytical data. When 0·01 mole of $K_6Cr(CN)_6$ was allowed to react with water a vigorous gas evolution was observed. This gas was carefully collected over acidified brine in an Orsat type apparatus. Acidified brine was used because it has a lower gas solubility coefficient than water. The gas was identified as hydrogen, and a volume of 319 ml at standard conditions of temperature and pressure was observed versus the calculated value of 336 ml if the reaction proceeded via the equation:

$$2K_6Cr(CN)_6 + 6H_2O \rightarrow 2K_3Cr(CN)_6 + 6KOH + 3H_2 \uparrow \quad (2)$$

A simple alkalimetric titration proved that three equivalents of base were produced for every mole of $K_6Cr(CN)_6$ reacted. The final solution had the yellow colour characteristic of $K_3Cr(CN)_6$. Since the latter compound is the salt of a strong base and a strong acid ($H_3Cr(CN)_6$), it would not interfere in a simple alkalimetric titration. The acid, $H_3Cr(CN)_6$, is a strong acid, yielding only one break in the titration curve for *three* equivalents of base used.[9]

Qualitative magnetic measurements by electron paramagnetic resonance indicate that the compound $K_6Cr(CN)_6$ is diamagnetic. This is to be expected of a zero valent chromium compound with $d^2sp^3$ hybridization as in chromium hexacarbonyl,[10] in which the 3d, 4s, and 4p levels are completely filled.

The final characteristic of $K_6Cr(CN)_6$ which can be described is the reaction with carbon monoxide, obtained either by bubbling the gas through a freshly precipitated slurry in liquid ammonia or under a variety of conditions of pressure and temperature, to form the air- and moisture-sensitive pale yellow potassium tricarbonyltricyanochromate(O), $K_3Cr(CO)_3(CN)_3$. This compound has been previously reported by HIEBER[1], who treated $Cr(CO)_3(NH_3)_3$ with a liquid ammonia solution of potassium cyanide. Either the stability of $K_3Cr(CO)_3(CN)_3$ with respect to chromium hexacarbonyl must be remarkably high or a high activation barrier must exist for the reaction, because the latter compound was never formed when carbon monoxide was allowed to react with $K_6Cr(CN)_6$, even under extreme conditions of pressure (2200 lb $in^{-2}$) and temperature (300°C) using several common co-ordinating organic solvents as, for example, di-*n*-butyl ether.

[9] J. BRIGANDO, *C. R. Acad. Sci., Paris* **208,** 197 (1939).
[10] W. KLEMM, H. JACOBI and W. TILK, *Z. Anorg. Chem.* **201,** 1 (1931).

The excellent agreement among the four independent strands of evidence described above may best be explained on the assumption that the green precipitate obtained from the reaction between potassium and potassium hexacyanochromate (III) in liquid ammonia at its boiling point contains chromium in the zero oxidation state. If this is correct, then the composition of the green precipitate is represented by the formula $K_6Cr(CN)_6$, potassium hexacyanochromate (O).

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# A SPECTROPHOTOMETRIC STUDY OF THE THORIUM-β-HYDRONAPHTHAZARIN DISULPHONATE* SYSTEM†

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**Abstract**—A spectrophotometric study of the reaction between thorium ion and β-hydronaphthazarin disulphonate (dipotassium 1,2,3,4-tetrahydro-5,8-dihydroxy-1,4-diketonaphthalene-2,6-disulphonic acid) in aqueous solution showed that two water-soluble complexes were formed, a green complex with a metal to ligand ratio of 1:1 and a blue complex with a metal to ligand ratio of 2:1. The green complex with an absorption maximum at 460 mμ was formed with β-hydronaphthazarin disulphonate, while the blue complex with absorption maxima at 570 and 610 mμ was formed with naphthazarin disulphonate. A study of the related thorium-β-hydronaphthazarin system indicated that complex formation does not occur unless conditions were such that the ligand was oxidized to naphthazarin.

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THE isolation of a pure, yellow, micro-crystalline solid formed in the reaction of naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) with potassium metabisulphite has been recently reported in the literature.[1] Although a water-soluble product from the reaction of naphthazarin and bisulphite was used at one time in the printing industry, it was described as a dark-brown powder and was thought to be the normal carbonyl bisulphite addition compound. The recent investigators, however, regard the purified material as the disulphonate derivative of β-hydronaphthazarin (1,2,3,4-tetrahydro-5,8-dihydroxy-1, 4-diketonaphthalene)‡ produced by the usual 1,4 quinoid addition. The product, isolated as the dipotassium salt, has the formula $C_{10}H_6O_{10}S_2K_2$. In view of the lengthy systematic name for the naphthazarin-bisulphite adduct, we have chosen to call it β-hydronaphthazarin disulphonate, abbreviated for convenience, β-HND.

Prior to this investigation, the complexes of naphthazarin which have been studied spectrophotometrically were those of beryllium[2,3], thorium[4] and some rare earth metal ions.[5] With beryllium, two complexes were formed; one in which the ratio of metal to ligand is 1:1, and in the other, 1:2; with thorium, however, only one complex was reported in which the ratio of metal to ligand is 1:2. The rare earth complexes exhibit the same properties as the thorium complex and have the

* Authors' name for the dipotassium salt of 1,2,3,4-tetra-hydro-5,8-dihydroxy-1,4-diketonaphthalene-2, 6?-disulphonic acid. The place of the second sulphonic acid group is not certain but is thought to be at the six position.

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‡ The sulphonation of quinones with bisulphite results in the reduction of the quinoid nucleus.

[1] D. B. BRUCE and R. H. THOMSON, *J. Chem. Soc.* 1089 (1955).
[2] T. Y. TORIBARA and A. L. UNDERWOOD, *Analyt. Chem.* **21**, 1348 (1949).
[3] A. L. UNDERWOOD, T. Y. TORIBARA and W. F. NEUMAN, *J. Amer. Chem. Soc.* **72**, 5597 (1950).
[4] T. MOELLER and M. TECOTSKY, *Analyt. Chem.* **27**, 1056 (1955).
[5] T. MOELLER and M. TECOTSKY, *J. Amer. Chem. Soc.* **77**, 2649 (1955).

same metal to ligand ratio. All the complexes were colloidal and the 1:1 beryllium complex, the thorium complex, and the rare earth complexes were thought to be polymeric. The investigations were carried out in either alcohol–water medium or dioxane–water medium because of the extremely low solubility of naphthazarin in water.

In view of these facts, it was considered appropriate to investigate the use of water-soluble β-HND as a chromogenic agent for thorium in the hope of obtaining a water-soluble and possibly non-colloidal complex. Also of interest was the effect, if any, of the sulphonic acid groups on the nature of the complex, as well as the effect of the reduced quinoid nucleus. In order to obtain additional information which was needed for a more complete understanding of the β-HND system, the thorium–β–hydronaphthazarin system was studied and the thorium–naphthazarin system re-investigated.

## EXPERIMENTAL

### *Chemicals and reagents*

All inorganic chemicals were reagent grade. Common organic solvents c.p. grade or better were used without further purification. High purity absolute ethanol obtained from Commercial Solvents Corporation, Terre Haute, Indiana, was used for spectrophotometric work requiring an organic solvent.

Naphthazarin was prepared according to the method of FIESER[6] and also purchased from the Aldrich Chemical Company. Irrespective of its source, the naphthazarin was quite crude and required extensive purification. Pure naphthazarin was obtained by extracting the crude material with skellysolve E (b.p. 100–120°C) using a Soxhlet extractor and recrystallizing the product from skellysolve containing a small amount of decolourizing carbon.

β-hydronaphthazarin was prepared by reduction of naphthazarin with acid stannous chloride according to the procedure of BRUCE and THOMSON.[7]

β-hydronaphthazarin disulphonate (β-HND) was prepared by sulphonation of naphthazarin with potassium metabisulphite according to the method of BRUCE and THOMSON.[1] Unless extremely pure naphthazarin was used for this preparation, the product was a dark-brown powder which did not give the correct elemental analysis.

An approximately 0·1 molar stock solution of thorium was prepared by dissolving a quantity of thorium nitrate tetrahydrate (Fisher Scientific Company) in distilled water. The solution was standardized gravimetrically by precipitation with ammonium hydroxide followed by ignition of the hydroxide to thorium oxide.[8] Solutions of thorium, 0·0024 molar, used in the spectrophotometric studies were prepared by quantitative dilution of aliquots from this stock solution.

Solutions of naphthazarin and β-hydronaphthazarin, 0·0024 molar, were prepared by dissolving weighed amounts of the respective reagents in absolute ethanol. Solutions of β-HND, 0·0024 molar, were prepared by dissolving weighed amounts of the reagent in distilled water.

### *Instruments and measurements*

All pH measurements were made with a Leeds and Northrup pH meter, number 7664, using the Leeds and Northrup miniature pH electrode assembly. All absorption spectra measurements were made with a Beckman Model DU quartz spectrophotometer, a Cary Model 14 recording spectrophotometer, or a Perkin-Elmer Model 4000 recording spectrophotometer using 1·00 cm matched quartz cells.

### *Experimental procedure*

For studies of the colour-forming reagents, solutions of the proper concentration for spectrophotometric work (approximately $10^{-4}$ to $10^{-5}$ molar) were prepared in 50 ml volumetric flasks by

[6] L. FIESER, *J. Amer. Chem. Soc.* **50**, 460 (1928).
[7] D. B. BRUCE and R. H. THOMSON, *J. Chem. Soc.* 2759 (1952).
[8] W. F. HILLEBRAND and G. E. F. LUNDELL, *Applied Inorganic Analysis*, (2nd Ed.) p. 542. J. Wiley, New York (1953).

dilution of varying amounts of 0·0024 M stock solutions with the appropriate solvent. For studies involving the formation of metal-reagent complexes, aliquots of the appropriate 0·0024 M stock solutions were mixed in 50 ml volumetric flasks and diluted to volume. Aliquots of the stock solutions were measured with 10 ml microburettes. Adjustments of pH, when required, were made with 0·1 N hydrochloric acid and 0·1 N sodium hydroxide. Buffer solutions of the CLARK and LUBS type[9] were also used to adjust pH.

*Composition studies*

*Method of continuous variation.*[10] For this method varying volumes of $2{\cdot}4 \times 10^{-3}$ molar solutions in a total volume of 50 ml were used. The total concentration was maintained constant at $4{\cdot}8 \times 10^{-4}$ molar. Reagent blanks were used as a reference. The colour of the blue species was developed by heating a concentrated mixture of metal and ligand at 60°C for 1 hr before dilution to volume. The acidity of all solutions was conveniently adjusted to pH 2·6 by adding 10 ml of Clark and Lubs buffer of pH 2·0.

The method of continuous variations was also applied in confirming the composition of the complex in the thorium–naphthazarin system and in determining the composition of the species in the thorium-β-hydronaphthazarin system. Varying amounts of $2{\cdot}4 \times 10^{-3}$ molar metal and ligand solutions were mixed and diluted to 50 ml with ethanol for these studies. Reagent blanks were used as reference.

*Slope-ratio method.*[11] For the determination of the empirical formula of the blue complex in the thorium–β–HND system by this method, two sets of solutions were prepared by mixing varying aliquots of $2{\cdot}4 \times 10^{-3}$ molar solutions and diluting to a total volume of 50 ml. For the set in which the concentration of thorium was held constant, absorbance readings were measured against a water blank, while for the second set a reagent blank was used. The colour of the complex was developed by heating the concentrated mixture for 1 hr at 60°C and the pH of all solutions was adjusted to 2·6 by adding 10 ml of Clark and Lubs buffer of pH 2·0. Plots of absorbance versus concentration of varying component were made at several wavelengths in the 570–620 mμ range. The formula of the complex was then calculated from the ratio of the slopes of the straight line portions of the curves.

A similar procedure was used to find the formula of the green complex in the thorium–β–HND system except that in this instance the solutions were not heated and the pH was adjusted to 3·0 with buffer. Absorbance readings for both sets of solutions were taken against reagent blanks.

*Mole-ratio method.*[12] Two sets of solutions were used to determine the formula of each species by this method. The concentration of constant component was $9{\cdot}6 \times 10^{-5}$ molar. For the blue species the pH was adjusted to 2·6 and for the green species the pH was adjusted to 3·0. Spectra were obtained using reagent blanks as reference. Plots of absorbance versus mole-ratio were obtained at the wavelengths of maximum absorbance to determine the composition of the complexes.

## RESULTS AND DISCUSSION

### *Nature and stability of β–HND solutions*

Aqueous solutions of β-HND which were initially pale-yellow turned red on standing even if put in stoppered bottles and stored in the dark. A study of the absorption spectra of several of these solutions showed that on standing there was a decrease in absorbance at 405 mμ, the wavelength of maximum absorbance for β-HND, and an increase in the region from 480 to 560 mμ. This behaviour is shown in Fig. 1. The change to red was slow but could be hastened somewhat by heating or by allowing the solution to be aged under alkaline conditions. It was possible to prevent any colour change by adding a small amount of potassium metabisulphite (0·1 g per 100 ml) to the stock solutions. Solutions to which metabisulphite had been

[9] W. M. CLARK and H. A. LUBS, *J. Biol. Chem.* **25**, 479 (1916).
[10] P. JOB, *Ann. Chim.* **9**(10), 113 (1928); W. C. VOSBURG and G. F. COOPER, *J. Amer. Chem. Soc.* **63**, 437 (1941).
[11] A. E. HARVEY and D. L. MANNING, *J. Amer. Chem. Soc.* **72**, 4488 (1950).
[12] J. H. YOE and A. L. JONES, *Industr. Engng. Chem. Analyt. Ed.*, **16**, 111 (1944).

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added were stored for more than one month with no significant change in absorbance at 405 m$\mu$. Since, however, no quantitative study of this change was made, it is not possible to state the rate of conversion, nor the degree of conversion.

From such behaviour it is believed that in untreated solutions $\beta$-HND undergoes slow air oxidation to naphthazarin disulphonate, ND. This view is supported in that aged reagent is red in colour and absorbs in the same region of the spectrum as naphthazarin as has been shown in Fig. 1.

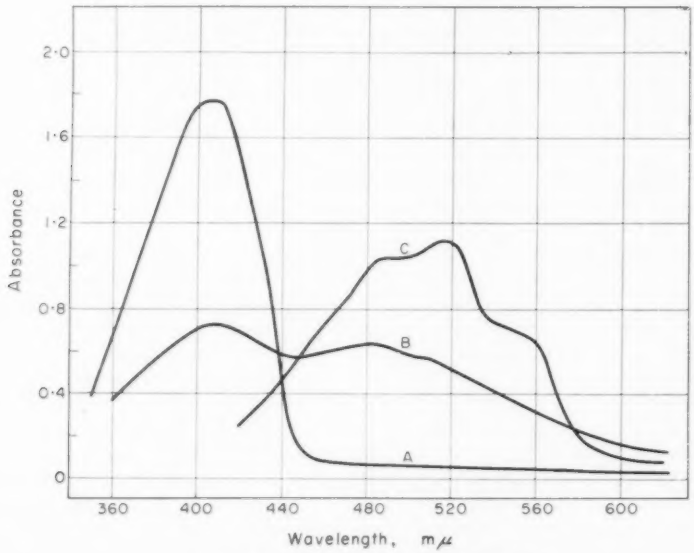


Fig. 1.—Absorbance vs Wavelength, m$\mu$
Absorption spectra
A. $2{\cdot}4 \times 10^{-4}$ M$\beta$-HND freshly prepared
B. $2{\cdot}4 \times 10^{-4}$ M$\beta$-HND aged 10 weeks
C. $2{\cdot}4 \times 10^{-4}$ M naphthazarin in ethyl alcohol.

The addition of sodium hydroxide caused the pale-yellow solutions to change slowly from brown to green to deep-blue. The deep-blue alkaline solution has an absorption spectrum characterized by a broad absorption maximum in the region of 630 m$\mu$. Naphthazarin in alkaline solution gives a similar spectrum. Neutralization of the alkaline $\beta$-HND solution produced a red solution with an absorption spectrum similar to those obtained from aged aqueous solutions. Apparently the oxidation of the molecule occurs more readily in alkaline solution.

*Spectrophotometric study of the thorium–$\beta$-HND system*

The absorption spectra from a study in which the ratio of metal to reagent was varied from greater than one to less than one, with the concentration of reagent held constant, showed absorption maxima in the region of 460, 570 and 610 m$\mu$. Solutions of the complexes containing reagent in excess were light-green when freshly prepared but slowly turned blue on standing. The corresponding absorption spectra (Fig. 2) showed that in the freshly prepared solution only one complex, a green complex with an absorption maximum at 460 m$\mu$ was formed as indicated by curve *A*, but on

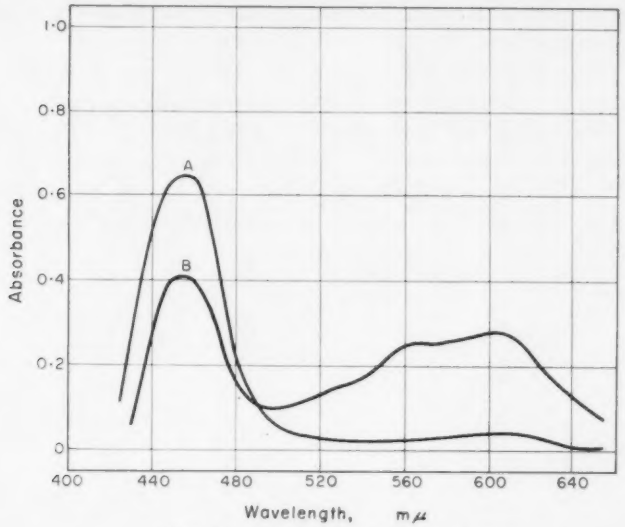


FIG. 2.—Absorbance vs Wavelength, mμ
Absorption spectra of thorium-β-HND system showing change in nature of complex with time.
Ratio of metal to reagent is 1:2
A. complex freshly prepared
B. complex aged 20 hr.

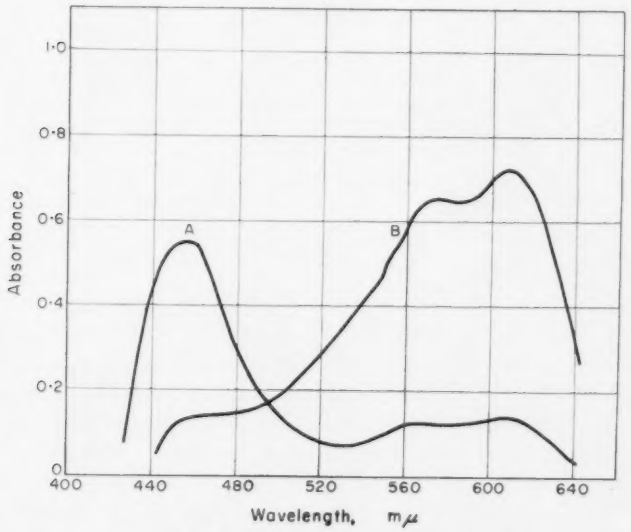


FIG. 3.—Absorbance vs Wavelength, mμ
Absorption spectra of thorium-β-HND system showing change in nature of complex with time.
Ratio of metal to reagent is 2:1
A. complex freshly prepared
B. complex aged 22 hr.

standing, a blue species (curve *B*) with absorption maxima at 570–610 mμ appeared. Solutions of the complexes containing thorium in excess were also light-green on first mixing but rapidly turned blue on standing. The corresponding absorption spectra (Fig. 3) showed that in the freshly prepared solution both green and blue

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species were present (curve *A*). On standing, however, conversion to blue species was almost complete (curve *B*).

From behaviour such as this, it appears reasonable that the green species is the result of complex formation with β-HND, while the blue species is the result of complex formation with ND. Since aqueous solutions of β-HND are unstable towards oxidation and contain both β-HND and ND, this explanation would appear to be reasonable. Furthermore, when complexes were prepared using reagent which had been allowed to age, both green and blue species were formed immediately.

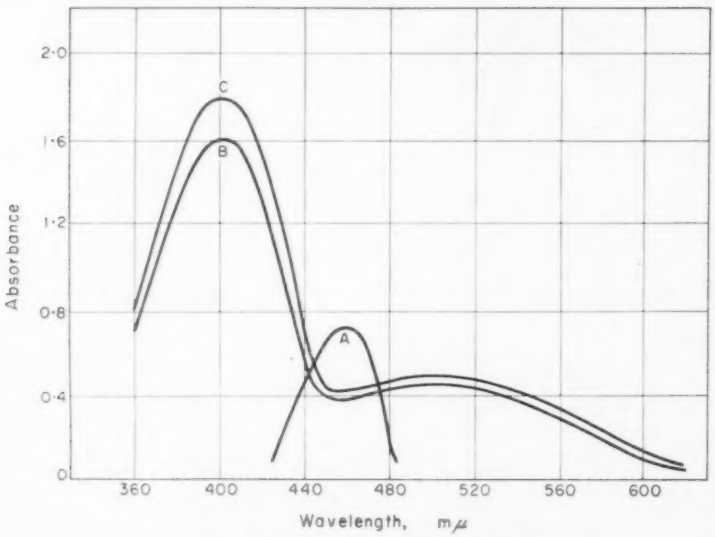


FIG. 4.—Absorbance vs Wavelength, mμ
Absorption spectra of thorium-β-HND system showing nature of reagent in 1:1 complex
A. thorium–β-HND complex against reagent blank
B. complex broken with dilute nitric acid, water blank
C. β-HND against water blank.

To support the view that the two species were a result of complex formation with β-HND and ND a series of tests were conducted in which the aqueous solutions of β-HND and thorium–β-HND mixtures were stabilized by the addition of potassium metabisulphite. An examination of the absorption spectra of complexes prepared in this manner revealed that the green complex with absorption maximum at 460 mμ was the only complex which formed. Even heating the solutions for one hour at 60°C failed to promote the formation of even a trace of blue species. Moreover, as shown in Fig. 4, when dilute nitric acid was added to a solution containing green complex in order to free the reagent, the absorption spectrum of the resulting yellow solution was identical with that for β-HND.

In order to further substantiate the conclusion that the blue species was the result of complex formation with ND, dilute nitric acid was added to a solution containing only the blue species. As shown in Fig. 5, the spectrum of the resulting red solution containing freed reagent was similar to that expected for ND.

Solutions of the green and blue complexes are colloidal in nature since both show

a Tyndall effect when placed in the beam of a strong light. The reagent alone, however, also shows a Tyndall effect and yet is extremely soluble in water. Apparently the hydrophilic nature of the sulphonic acid groups is sufficient to prevent flocculation of the reagent and its complexes.

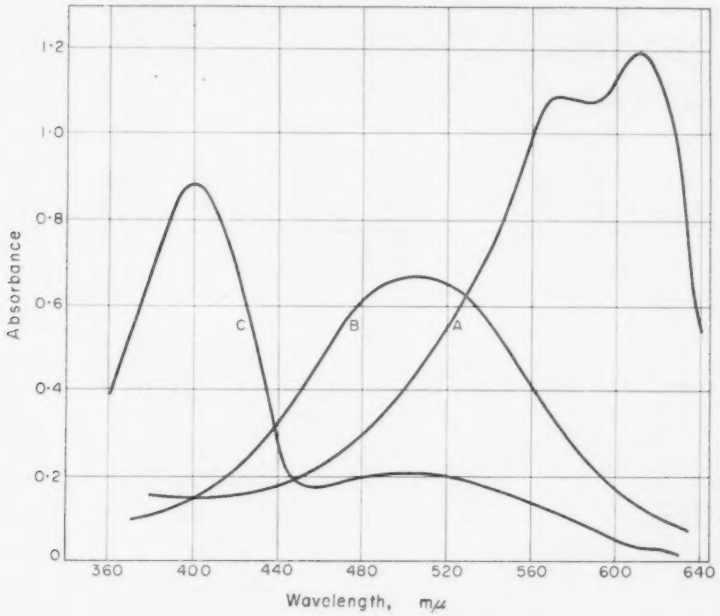


FIG. 5.—Absorbance vs Wavelength, mμ
Absorption spectra of thorium-β-HND system showing nature of reagent in 2:1 complex
A. thorium–β-HND complex with thorium in excess
B. complex broken with dilute nitric acid
C. $2{\cdot}4 \times 10^{-4}$ M β-HND.

TABLE 1.—EFFECT OF THE TIME OF STANDING ON UNHEATED SOLUTIONS

| Thorium concentration (M) | Absorbance (610 mμ) | | |
|---|---|---|---|
| | 24 hr | 120 hr | 144 hr |
| $4{\cdot}8 \times 10^{-5}$ | 0·114 | 0·151 | 0·151 |
| $9{\cdot}6 \times 10^{-5}$ | 0·285 | 0·324 | 0·323 |

*Formation of the complexes*

*Time study.* The effect of time of standing at room temperature on the observed absorbance for solutions of the blue complex prepared by mixing aliquots of metal and reagent in the two to one ratio as found in the complex and diluting to volume, is shown in Table 1. A comparison of these data with the absorbance values listed in Table 2 for solutions of the blue complex prepared by heating a concentrated two to one mixture of metal and reagent for one hour at 60°C before dilution to volume shows that heating not only promotes the rate of formation of the blue species but

also slightly increases the amount of complex formed. The values in Table 2 also indicate that the blue species is stable up to 72 hr; longer periods were not investigated. It should be emphasized that the values are for metal and reagent mixed in the two to one ratio corresponding to the composition of the complex. Solutions containing

Table 2.—Effect of the time of standing on solutions heated 1 hr at 60°

| Thorium concentration (M) | Absorbance (610 mμ) | | | |
|---|---|---|---|---|
| | 1 hr | 2 hr | 14 hr | 72 hr |
| $4{\cdot}8 \times 10^{-5}$ | 0·166 | 0·169 | 0·169 | 0·169 |
| $9{\cdot}6 \times 10^{-5}$ | 0·332 | 0·335 | 0·339 | 0·342 |

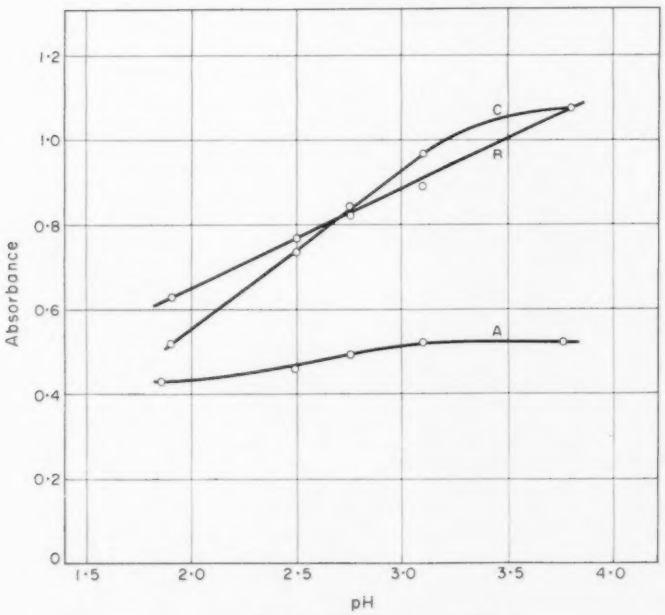


Fig. 6.—Absorbance vs pH
pH study of thorium–β-HND system
A. 460 mμ, 1:1 complex
B. 575 mμ, 2:1 complex
C. 610 mμ, 2:1 complex.

reagent in excess of this ratio show a gradual steady increase in absorbance on standing. This increase is attributed to the further oxidation of excess β-HND present in the solutions since oxidized reagent, ND, absorbs in the same region as the blue complex and, therefore, contributes to the observed absorbance.

*Effect of* pH. A study of pH effects indicated that common buffers decrease complex formation. Another study was made by adjusting the pH with dilute hydrochloric acid or sodium hydroxide. As indicated in Fig. 6, absorbance for the blue complex increases linearly with pH in the range 1·9–4·0. Although not shown in Fig. 6, above pH 4·0 the absorbance gradually decreases. In instances where

the pH was above 3·5, solutions containing blue complex had a tendency to leave blue stains on the absorbance cells and the sides of the volumetric flasks. Below pH 3·5 this difficulty was not encountered. The tendency of the complex to precipitate may be the result of hydrolysis since thorium hydroxide precipitates at a pH of 3·5.[13]

Absorbance for the green complex gradually increases with increased pH from 2 to 3 and is essentially constant in the range 3·0–4·0. Above pH 4·2 the complex appears to flocculate but attempts to isolate the solid complex were not successful.

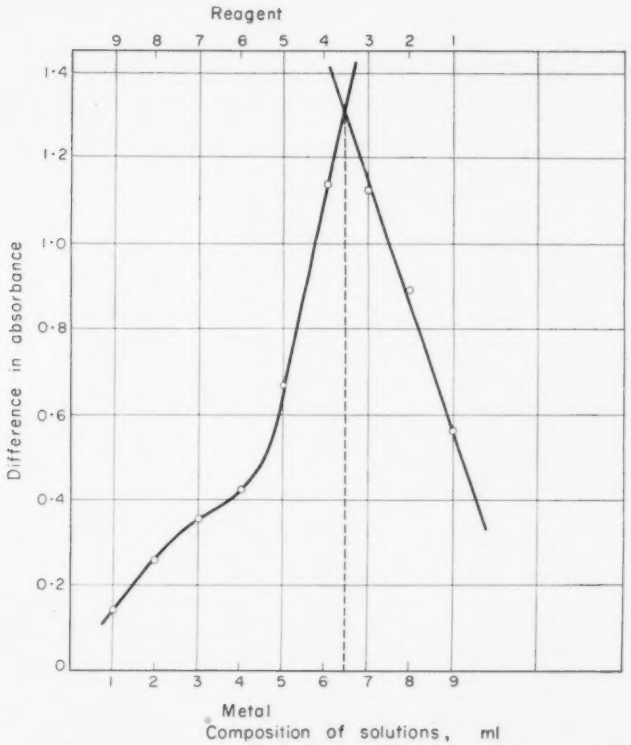


FIG. 7.—Difference in absorbance vs composition of solutions in ml
Continuous variations study on thorium-β-HND system at 610 mμ.

Since control of final pH was desirable, it was found convenient to make all pH adjustments with varying amounts of Clark and Lubs buffer of pH 2·0. A study indicated that absorbance values were essentially constant with potassium chloride in concentrations up to 0·2 molar. Higher salt concentrations were not investigated.

*Composition of the complexes*

All three methods, continuous variations, slope-ratio, and mole-ratio, used to determine the composition of the complexes indicated a 2:1 ratio of thorium to ND for the blue species and a 1:1 ratio of thorium to β-HND for the green species.

The sharp break in the curve shown in Fig. 7 indicates the 2:1 ratio obtained for the blue species by applying the method of continuous variations at 610 mμ. Similar

[13] J. J. FRITZ and J. J. FORD, *Analyt. Chem.* **25**, 1640 (1953).



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plots, which are not presented, at wavelengths in the 560–620 m$\mu$ region demonstrated further the 2:1 ratio of metal to ligand for the blue species.

The curve shown in Fig. 8 is from the mole-ratio study and indicates the 1:1 ratio of metal to ligand found for the green species at 460 m$\mu$. Additional continuous variation plots, mole-ratio plots, as well as the slope-ratio plots, which are not presented here confirm the compositions of the blue and green species.

In the mole-ratio study, plots of absorbance versus composition for solutions containing metal in excess indicated the same composition as plots made from solutions containing reagent in excess. It is reasonable, therefore, to conclude that the

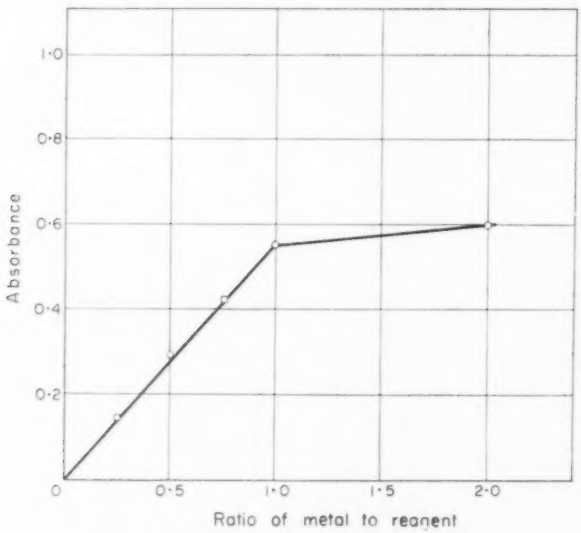


FIG. 8.—Absorbance vs ratio of metal to reagent
Mole ratio study of thorium–$\beta$-HND system at 460 m$\mu$, thorium varying.

2:1 blue complex and the 1:1 green complex are the only complexes which exist in the respective systems.

It might be pointed out that earlier in the work, before it was realized that the two absorbing species were the result of two different forms of the reagent, care was not taken to prevent the formation of the blue species. As a consequence, when the mole-ratio study was undertaken to determine the composition of the green complex, interference from the formation of the blue species caused a sharp decrease in the measured absorbance at 460 m$\mu$ which was then erroneously interpreted as suggesting a 1:2 ratio of metal to ligand for the green complex. What had actually occurred was that the presence of the blue species had reduced the overall amount of the green species present. The break in the curve, therefore, instead of being indicative of the composition of the complex, was merely a departure from Beer's law due to the decreased formation of the green complex. When in later experiments, care was taken to prevent the formation of blue species either by the addition of metabisulphite or by making the absorption measurements promptly after mixing the reactants, the 1:1 ratio of metal to ligand was observed.

*Adherence to Beer's law*

Conformity to Beer's law was observed for both species at the wavelengths of maximum absorbance. For the green species at pH 3·0 and wavelength 460 mμ, the average molar absorptivity was 6289 ± 33 for thorium concentrations between 2·4 and 12·0 × $10^{-5}$ M. Reagent in concentrations up to 4–1 (mole-ratio of reagent to metal) had little effect on the measured absorbance for solutions 2·4 × $10^{-5}$ M in thorium.

For the blue species at pH 2·6, and a metal to reagent ratio of 2:1, the average molar absorptivity was 3256 ± 86 at 575 mμ and 3374 ± 136 at 610 mμ for thorium concentrations between 2·4 to 33·6 × $10^{-5}$ M.

*Spectrophotometric determination of the degree of dissociation and instability constants for the green and blue species*

The spectrophotometric method employed for the determination of the instability constants depends upon the assumed formulas of the complexes as determined by the composition studies. The method used was that of HARVEY and MANNING[11]. Application of this method to the green species at 460 mμ for two sets of data at a complex concentration of 9·6 × $10^{-5}$ M and pH 3·0 gave values of 5·8 × $10^{-7}$ and 3·1 × $10^{-7}$ for the instability constant with respect to thorium ion and β-HND. For the blue species at 610 mμ two sets of data at a complex concentration of 4·8 × $10^{-5}$ M and pH 2·6 gave values of 2·2 × $10^{-10}$ and 7·6 × $10^{-10}$ for the instability constant. The values for the instability constants while indicating the relative stability of the green and blue complexes are rendered somewhat inaccurate by the colloidal nature of the species.

*Reinvestigation of the thorium–naphthazarin system*

The thorium–naphthazarin system was reinvestigated in order to determine if more than one complex could be present in solution. The continuous variation curve as reported by MOELLER and TECOTSKY[4] tends to be slightly concave at high thorium concentrations and thus another species may be present other than the one reported. Upon repeating the continuous variation study, as well as a mole-ratio study, only one absorbing species, the one to two, was found. The anomaly in the curve is probably a result of a departure from Beer's law since MOELLER and TECOTSKY point out that solutions of complex containing naphthazarin in quantities less than the stoichiometric one to two ratio deviate markedly from Beer's law.

*Study of the thorium–β-hydronaphthazarin system*

In order to learn what effect reduction of the quinoid nucleus of naphthazarin would have on complex formation, a study of the thorium–β-hydronaphthazarin system was undertaken.

The system was studied by mixing aliquots of the stock solutions of metal and reagent in the usual manner. Absorption spectra of solutions containing a mixture of metal and ligand were identical, however, to spectra for the reagent alone, indicating that complex formation did not occur. Even heating the diluted solutions for 1 hr at 60°C failed to promote any significant complex formation. This is unlike the thorium-naphthazarin system in which a purple complex forms immediately, and also unlike the thorium–β-HND system in which the green complex forms immediately.

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A purple complex was finally obtained by heating a concentrated mixture of thorium and β-hydronaphthazarin for 44 hr, but it was evident from a study of the absorption spectra that such prolonged heating had caused oxidation of the β-hydronaphthazarin to naphthazarin so that the observed complex was actually with naphthazarin and not β-hydronaphthazarin.

This view is supported by the fact that β-hydronaphthazarin reagent blanks were quantitatively oxidized to naphthazarin during the heating period. In addition, the spectrum of the resulting complex is similar to, and absorbs in the same region as, the complex prepared from naphthazarin. Moreover, when dilute nitric acid was added to free the reagent, the resulting red solution (β-Hydronaphthazarin solutions are yellow) had an absorption spectra identical to naphthazarin.

The ratio of thorium to reagent in the complex formed with β-hydronaphthazarin as starting material, as determined by the method of continuous variations, is 1:1. This is an unexpected composition since in the thorium-naphthazarin system only the 1:2 metal to ligand complex is formed, even when the solutions were heated for 44 hr. The reason for this composition is not clear at this time. One speculation might be that since the complex is apparently forming as the ligand molecule is oxidizing, a stable polymeric 1:1 species is actually formed. Such an explanation is not unreasonable since it has been already shown that naphthazarin can form polymeric species.[2–5]

## CONCLUSIONS

From a consideration of the results obtained on complex formation in the systems β-hydronaphthazarin and β-hydronaphthazarin disulphonate, it would appear that the green complex formed in the latter system is the result of co-ordination through functional groups other than those responsible for complex formation with naphthazarin. It may be that co-ordination takes place through hydroxyl oxygen and a sulphonic acid group. Co-ordination in which the sulphonic acid groups participate has also been proposed for the 2,7-dinitroso-1, 8-dihydroxynaphthalene-3,6-disulphonic acid complex with thorium.[14] The 2:1 ratio of metal to ligand in the case of the blue complex in the sulphonated reagent system may also be the result of the close proximity of the sulphonic acid groups to the other functional groups of the molecule. A study of the infra-red spectra of the solid complexes could help to understand the nature of the bonding in the complexes. However, all attempts to date to isolate the solid complexes have been unsuccessful.

The β-hydronaphthazarin system is interesting in that one would not have predicted that chelation would not take place. Although the reason for this failure to chelate is not understood at this time, the following explanation is suggested.

Since reduction of the quinoid nucleus decreases electron delocalization in the molecule, the tendency to chelate may also be decreased. Copper(II), for example, is known to form a stable chelate with acetylacetone but does not chelate with 4-hydroxypentanone-2.[15] The acetylacetonate chelate can be stabilized through resonance whereas with 4-hydroxypentanone-2 resonance stabilization is not possible. Similarly, FREISER[16] has demonstrated the influence of aromatic resonance in the case of divalent metal chelates of 8-hydroxyquinoline and 1,2,3,4-tetrahydro-8-hydroxyquinoline. The fact that the tetrahydro-8-hydroxyquinoline forms chelates

[14] S. K. DATTA, *Analyt. Chim. Acta* **15**, 415, 421 (1956).
[15] E. S. GOULD, *Inorganic Reactions and Structure*, p. 33. H. Holt, New York (1955).
[16] H. FREISER, *Analyst* **77**, 830 (1952).

that are considerably less stable than those of oxine despite the increase in basicity of its nitrogen (and to a lesser degree its phenolic oxygen) strengthens the view that resonance plays an important role in chelate formation. This decrease in aromatic resonance may well be an important factor in the non-chelating behaviour shown by β-hydronaphthazarin. In addition to the resonance factor, moreover, there may also be steric factors to consider. Whereas the naphthazarin molecule is planar, the β-hydronaphthazarin molecule in most likely non-planar. An examination of a model of this molecule shows that the saturated ring can assume chair and boat configurations similar to those found in *cyclo*hexane and *cyclo*hexanone. The non-planarity of this type of configuration might conceivably result in a large enough separation of the functional groups, carbonyl and phenolic, which are responsible for chelation, that a six-membered ring cannot be formed. This steric factor together with the overall decrease in resonance energy may account for the failure of β-hydronaphthazarin to chelate with thorium.

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# PREPARATION AND ALCOHOLYSIS OF *BIS*-(ETHYL-2,4-HEXADIENOATE)-DICARBONYL-MOLYBDENUM

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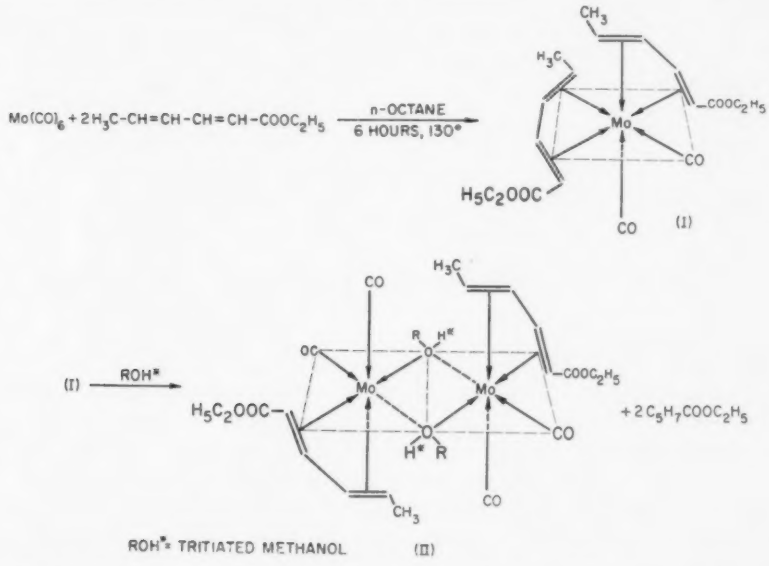
**Abstract**—The reaction of molybdenumhexacarbonyl with ethylsorbate afforded diamagnetic *bis*-(ethyl-2,4-hexadienoate)-dicarbonyl-molybdenum(O). Alcoholysis of the mononuclear complex with methanol, ethanol and benzylalcohol yielded binuclear di-$\mu$-alcohol bridged complexes whose structure was elucidated using radioactive tracer techniques. *Bis*-(ethyl-2,4-hexadienoate)dicarbonyl-tungsten could be synthesized analogously but was stable towards primary alcohols.

A NUMBER of diene- and polyene-substituted molybdenumcarbonyl compounds have been prepared in the recent past. With 2,2,1-bicycloheptadiene[1] and 1,5-cyclo-octadiene[2] as well as with more exotic hydrocarbons such as 7,8-dimethyl-tricyclo-[4,2,2,0] decadiene(3,9)[3], molybdenumcarbonyl forms tetracarbonyl compounds containing one diene per molecule. Most of the numerous tricarbonyl compounds described belong to the class of *cyclo*pentadienyl- and $\pi$-arene compounds,[4] but a few were reported where the $Mo(CO)_3$ moiety is bonded to other carbocyclic polyenes such as *cyclo*heptatriene,[5] 1,3,5-*cyclo*-octatriene[6] and azulene.[7] Four moles of carbon monoxide are replaced by the reaction of $Mo(CO)_6$ with 1,3,6-*cyclo*-octatriene[6] and with 1,3-cyclohexadiene,[8] giving rise to the respective dicarbonyl derivatives. All of these unsaturated hydrocarbon ligands forming mixed metal–olefin complexes with molybdenum or, for that matter, with its congeners, have carbocyclic structures. Only very recently was the synthesis of *bis*-butadiene-dicarbonyl-molybdenum reported by FISCHER *et al.*[9] These authors described the photochemically catalysed reaction of $Mo(CO)_6$ with butadiene to produce $(C_4H_6)_2Mo(CO)_2$ which also was obtained, in higher yield, by displacing the aromatic ligand and one CO from mesitylene-tricarbonyl-molybdenum. This communication prompts us to report some work we have done in this area, resulting in the formation of *bis*-diene-dicarbonyl complexes of molybdenum and tungsten from the respective hexacarbonyls and ethyl-2,4-hexadienoate.

[1] R. PETTIT, *J. Amer. Chem. Soc.* **81**, 1266 (1959).
[2] a. E. O. FISCHER and W. FROEHLICH, *Ber. Dtsch. Chem. Ges.* **92**, 2995 (1959).
b. T. A. MANUEL and F. G. A. STONE, *Chem. Industr.* 1349 (1959).
c. M. A. BENNETT and G. WILKINSON, *Chem. Industr.* 1516 (1959).
[3] M. AVRAM, E. SLIAM and C. D. NENITZESCU, *Liebigs Ann.* **636**, 184 (1960).
[4] See the recent reviews by:
a. F. A. COTTON, *Progress in Inorganic Chemistry*, Vol. 1, Chap. 1, Academic Press, New York (1959).
b. E. O. FISCHER and H. P. FRITZ, *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 1, pp. 55–115. (Edited by H. J. EMELEUS and A. G. SHARPE) Academic Press, New York (1959).
c. H. ZEISS, *Organometallic Chemistry*, American Chemical Society Monograph No. 147, Reinhold, New York (1960).
[5] E. W. ABEL, M. A. BENNETT, R. BURTON and G. WILKINSON, *J. Chem. Soc.* 4559 (1958).
[6] E.O. FISCHER and C. PALM, *Z. Naturforschg.* **14** b, 347 (1959); *Ber Dtsch. Chem. Ges.* **92**, 2645 (1959).
[7] R. BURTON and G. WILKINSON, *Chem. Industr.* 1205 (1958). *J. Chem. Soc.* 4209 (1960).
[8] E. O. FISCHER and W. FROEHLICH, *Z. Naturforschg.* **15** b, 266 (1960).
[9] E. O. FISCHER, H. P. KÖGLER and P. KUZEL, *Ber. Dtsch. Chem. Ges.* **93**, 3006 (1960).

The reaction of molybdenumhexacarbonyl with excess ethylsorbate, which proceeded smoothly without irradiation of the mixture, was carried out in boiling *n*-octane. Carbon monoxide was evolved and the filtered solution afforded a yellow crystalline solid in about 30 per cent yield after repeated recrystallization from cold methanol. This compound, (I), exhibited, in its infra-red spectrum, CO bands in the metal carbonyl region at 1923 and 1980 $cm^{-1}$ as well as an absorption at 1672 $cm^{-1}$ which is characteristic of the carboxy carbonyl group. Analysis of (I), which was found to be monomolecular in benzene, revealed its composition as $C_{18}H_{24}MoO_6$. These analytical and spectroscopical data as well as the established diamagnetism and

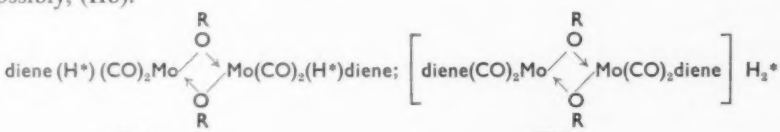



the reactive behaviour, which will be discussed in more detail, suggest the structure for (I) as *bis*-(ethyl-2,4-hexadienoate)-dicarbonyl-molybdenum(O). The multiplicity of its infra-red absorption in the metal carbonyl region indicates a *cis*-position of the two CO groups which has also been proposed for the *bis*-butadiene derivative, the latter exhibiting virtually identical CO stretching frequencies.[9] (I) was stable in air and melted, with decomposition, at 114–115·5°. When heated in its methanolic solution, (I) was found to undergo an apparently irreversible change and a methanol-insoluble solid, (II), was formed and isolated in about 60 per cent yield. Compound (II) differed in many respects from (I); it was distinctly less stable oxidatively, melted at 188–189°, with decomposition, and exhibited a different infra-red spectrum, the principal carbonyl bands being at 1812 and 1916 $cm^{-1}$ as well as at 1660 $cm^{-1}$.

This interesting alcoholysis reaction has been studied and sufficient evidence was accumulated to facilitate deduction of the structure of the product obtained. The analytical data for (II) were in agreement with Diene $Mo(CO)_2(CH_3OH)$. The molecular weight indicated a binuclear structure which was also to be expected based upon stereochemical considerations in order to achieve hexa-co-ordination. The dimeric structure is further supported by the diamagnetism of the solid. No hydrogen was evolved during alcoholysis. Using tritiated methanol, a product was isolated

which contained about 90 per cent of the employed activity per mole. Although this experiment clearly indicated that ROH* rather than $RO^-$ was incorporated in the binuclear structure, it does not furnish unequivocal proof with regard to the position of the labelled hydrogen. Based upon the available evidence it is not possible, therefore, to decide whether undissociated alcohol molecules or methoxy groups function as bridging moieties. In the first case, structure (II) would have to be formulated as *bis*-(ethyl-2,4-hexadienoate)-tetracarbonyl-di-$\mu$-methanol-dimolybdenum, as shown below.

If methoxy groups were to act as bridging links, structure (IIa), *bis*-(ethyl-2,4-hexadienoate)-tetracarbonyl-di-$\mu$-methoxy-dimolybdenum-dihydride, would be descriptive of the bonding relations, thus resembling the binuclear $\mu$-hydroxy and $\mu$-methoxy molybdenumcarbonyl hydrides which have recently been described.[10] From the insolubility of (II) in dilute aqueous $Na_2CO_3$ and NaOH solutions it is concluded that the hydrogen H* is not very acidic, as would be expected from (IIb). Nevertheless, we believe at the present time that the structure for the alcoholysis product, as far as the position of the labelled hydrogen is concerned, can be represented by (II), (IIa) or, possibly, (IIb).




(IIa) (IIb)

The reaction seems to be general as far as primary alcohols are concerned, the analogous compounds containing ethanol and benzylalcohol have been isolated. They were soluble in benzene, toluene, etc. From its benzene solution, the di-$\mu$-methanol complex crystallized as an adduct containing about 0·75 mole of benzene per metal (1·5 $C_6H_6$ per mol of the binuclear compound). It is probable, that the crystalline complex acts as the host compound for benzene, forming a clathrate. Rapid decomposition takes place when compound (II) is contacted with THF and similar solvents. This is probably due to displacement of the alcohol ligand and subsequent rupture of the binuclear structure if the displacing ligand cannot substitute for the displaced moiety as a bridging link, a penta-co-ordinated mixed metal carbonyl obviously not being capable of existence.

The described reaction may also exemplify the difference between the group VI transition metals as it frequently manifests itself in the dissimilar behaviour of homologous compounds. Whereas chromiumhexacarbonyl under the same conditions did not afford any substituted derivative (only some decomposition occurred), tungstenhexacarbonyl produced *bis*(ethyl-2,4-hexadienoate)-dicarbonyltungsten in about 21% yield. The attempted alcoholysis of this compound, however, met with failure; upon treatment with hot methanol, only the unreacted *bis*-diene-dicarbonyl could be recovered.

## EXPERIMENTAL

*Preparation of* bis(*ethyl*-2,4-*hexadienoate*)-*dicarbonyl-molybdenum*

The mixture of 13·2 g (0·05 mole) of $Mo(CO)_6$, 21·0 g (0·15 mole) of ethylsorbate, 65 ml of *n*-octane and a pinch of hydroquinone was heated, under nitrogen, to reflux (130°) for 6 hr during which time

[10] W. HIEBER, K. ENGLERT and K. RIEGER, *Z. Anorg. Chem.* **300**, 295 (1959). W. HIEBER, W. BECK and G. BRAUN, *Angew. Chem.* **72**, 800 (1960).

4·0 l. (s.t.p.) of gas were evolved. The resulting red solution was filtered hot, under a nitrogen atmosphere, from some greenish precipitate, using a glass fritted plate apparatus. After washing this solid residue well with hot *n*-octane, the volume of the combined filtrates was reduced to about 20 ml using a rotary evaporator. The yellow crystalline precipitate thus obtained was washed with petroleum ether and recrystallized twice from methanol at room temperature. The yield was 6·3 g (29·1%). The solubility of this compound in methanol at 25° was determined, by decomposition of an aliquot amount of saturated solution, to be 18·9 g/l. The compound was stable in air and soluble in benzene, ethanol, methanol, acetone, ether, tetrahydrofuran and *n*-octane, slightly soluble in petroleum ether and insoluble in water. It melted at 114–115·5° and was diamagnetic.* Its infra-red spectrum was taken in a KBr wafer and exhibited carbonyl bands at 1980, 1923 and 1672 $cm^{-1}$, the latter absorption being assigned to the carboxy carbonyl group. (Found: C, 50·3; H, 5·69; Mo, 22·0%, mol. wt. 437-(Cryoscopically, in benzene). Calc. for: $C_{18}H_{24}MoO_6$: C, 50·00; H, 5·60; Mo, 22·19%; mol. wt. 432·2). When heated to over 100° the compound could be sublimed with heavy losses due to partial decomposition (0·1 mm).

*Preparation of* bis(*ethyl*-2,4-*hexadienoate*)-*dicarbonyl-tungsten*

After refluxing the mixture of 8·8 g (0·025 mole) of $W(CO)_6$, 10·5 g (0·08 mole) of ethylsorbate, 40 ml of *n*-nonane and 10 ml of *n*-octane together with a pinch of hydroquinone for 12·5 hr (146–149°), during which time 1·6 l. (s.t.p.) of gas had been evolved, it was filtered hot and worked up as described above. After two recrystallizations from petroleum ether 2·7 g (20·8 per cent) of yellow crystalline solid were obtained. The compound melted at 116–117·5°, it was stable in air, soluble in benzene, methanol, ethanol, acetone, ether, tetrahydrofuran, carbon tetrachloride, petroleum ether and insoluble in water. It could be sublimed, with some decomposition, at 90°/0·1 mm and showed carbonyl stretching frequencies at 1976 and 1919 $cm^{-1}$, as well as a strong absorption at 1681 $cm^{-1}$, taken in $CCl_4$ solution. (Found: C, 41·5; H, 4·58; W, 34·6. Calc. for: $C_{18}H_{24}WO_6$: C, 41·51; H, 4·65; W, 35·35%). The compound was recovered unchanged after heating to reflux in methanol for 30 min; this was evidenced by the identity of infra-red spectrum and melting point.

*Preparation of* bis(*ethyl*-2,4-*hexadienoate*)-*tetracarbonyl-di-μ-methanol-dimolybdenum*

The clear yellow solution of 3·0 g (0·0068 mole) of (I) in 165 ml methanol was agitated and heated on a steam bath, under nitrogen, for 15 min. A yellow crystalline precipitate formed which was separated by filtration after gradually cooling the mixture to room temperature. After washing with methanol and drying the yield was 1·3 g (57·8 per cent). The compound melted at 188–189° and was soluble in benzene and acetone, slightly soluble in *n*-octane, petroleum ether and ethanol with a yellow colour; in ether, however, it dissolved giving a red solution. With tetrahydrofuran it reacted vigorously with gas evolution. The initially deep red solution thus formed assumed a greenish blue colour upon standing; its infra-red spectrum revealed only presence of a trace of $Mo(CO)_6$. The compound, which was insoluble in water as well as in dilute aqueous $Na_2CO_3$ and NaOH solutions, was diamagnetic and exhibited strong carbonyl absorptions in its infra-red spectrum at 1916, 1812 and 1656 $cm^{-1}$, taken from a KBr disk. (Found: C, 40·6; H, 5·06; Mo, 29·8%; mol. wt. 688·0. Calc. for: $C_{22}H_{32}Mo_2O_{10}$: C, 40·75; H, 4·97; Mo, 29·6%; mol. wt. 648)†. In order to ascertain the function of the methanol, the clear solution of 1·4 g (0·0032 mole) of (I) in 90 ml of methanol was cooled in liquid nitrogen and the reaction flask evacuated. The contents were then heated to reflux for 3 hr, during which time precipitation occurred. After cooling to −80°, no gas could be removed from the system by means of an attached Toepler-pump. This indicated that there was no hydrogen evolution accompanying the alcoholytical cleavage.

*Preparation of* bis(*ethyl*-2,4-*hexadienoate*)-*tetracarbonyl-di-μ-ethanol-dimolybdenum*

The filtered clear solution of about 1 g (0·002 mole) of (I) in 90 ml of ethanol was heated, under nitrogen, and stirred for 10 min on a steam bath. Although no precipitate came down, the colour of the solution deepened and upon reduction of its volume it afforded 0·3 g (38·5 per cent) of a yellow

* We are indebted to Professor S. KIRSCHNER at Wayne State University for carrying out the magnetic susceptibility measurements.

† Molecular weight determination was carried out using an isopiestic method (Signer). The high result, after four weeks running time in dichloromethane, may be explained by partial crosslinking of the bridged compound, giving rise to higher aggregated moieties.

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crystalline solid which was washed with ethanol and dried overnight in vacuum. The compound reacted vigorously with tetrahydrofuran, as did the methanol derivative; its infra-red spectrum was characterized by strong absorptions at 1912, 1808 and 1661 $cm^{-1}$. It melted at 175–176°. (Found: Mo, 28·57. Calc. for: $C_{24}H_{36}Mo_2O_{10}$: Mo, 28·37%).

*Preparation of* bis(*ethyl*-2,4-*hexadienoate*)-*tetracarbonyl-di-μ-(benzyl alcohol)-dimolybdenum*

The clear yellow solution of 1·5 g (0·0035 mole) of (I) in 40 ml of benzyl alcohol was heated and stirred on a steam bath for 20 min, under nitrogen. An oily residue resulted after removing most of the alcohol in vacuum; it was triturated with methanol (20 ml) and the yellow precipitate thus obtained was separated by filtration after cooling the mixture, and washed with cold petroleum ether. Recrystallization from dichloromethane/methanol afforded 0·2 g (14·4 per cent) of a yellow crystalline material melting at 160–161° with decomposition. This compound also reacted with tetrahydrofuran and exhibited infra-red absorption bands at 1923, 1825 and 1658 $cm^{-1}$. (Found: Mo, 24·3. Calc. for $C_{31}H_{10}Mo_2O_{10}$: Mo, 24·0%).

*Reaction of* bis(*ethyl*-2,4-*hexadienoate*)-*dicarbonyl-molybdenum with tritiated methanol*

In order to show that the hydroxylic hydrogen remained in complex (II), its preparation was repeated using methanol which had been tagged in the OH group. An exploratory run showed, that the methanol had to be anhydrous. Therefore, the mixture of about 1 per cent tritiated water in methanol was dried carefully by refluxing over iodine-activated magnesium turnings and subsequent distillation. The di-μ-methanol complex, (II), was prepared as outlined above, using 1 g of (I) in 65 ml of $CH_3OH^*$ and washing the formed precipitate with $CH_3OH^*$ of the same activity. The yield of nicely crystalline solid, (II), melting at 188–188·4°, was 0·2 g (28 per cent). The compound (II) was measured after drying for 20 hr at 25°/0·1 mm; the measurement was repeated after another 5 hr of drying under the same conditions. A Packard Tri-Carb liquid scintillation spectrometer was used to count the activities. The toluene phosphor was of a familiar DPO-POPOP formulation.

*Activity of* $CH_3OH^*$. The methanol (0·00623 mmole) produced a count of $86 \times 10^3$ counts/min. Since an internal standard of active toluene showed the efficiency was 14 per cent, the specific activity followed to be $4{\cdot}45 \times 10^{-2}$ mc/mmole.

*Activity of labelled compound* (II). In the same system, 0·92 mg of (II) produced a count of $12{\cdot}0 \times 10^3$ counts/min. The internal standard showed the efficiency of the (coloured) system to be now 4·87 per cent. The specific activity was, therefore, $7{\cdot}82 \times 10^{-2}$ mc/mmole. The repeat measurement made after the 5 hr drying was carried out with a sample of 1·07 mg. The efficiency was 4·82 per cent and the specific activity proved to be $8{\cdot}10 \times 10^{-2}$ mc/mmole.

The observed change in activity after the drying step was therefore not significant and the average of the two values results as $7{\cdot}96 \times 10^{-2}$ mc/mmole. This is about 90 per cent of the specific activity of the methanol employed. An isotope effect of at least some small magnitude was to be anticipated. The result thus furnished conclusive proof for the incorporation of $CH_3OH^*$ rather than the methoxy group $CH_3O^-$ into the binuclear cleavage product, (II).

*Reaction of* bis(*ethyl*-2,4-*hexadienoate*)-*tetracarbonyl-di-μ-methanol-dimolybdenum with benzene*

The volume of a filtered yellow solution of 0·2 g (0·31 mole) of (II) in 80 ml of benzene was reduced until fine shiny needles appeared. After cooling the mixture, the solid was filtered off, washed with cold benzene and dried for 3 hr at 25°/0·1 mm, The compound which melted at 179–180° was air-sensitive and reacted with tetrahydrofuran; its infra-red spectrum was identical with the one taken from (II); the yield was 0·15 g. (Found: C, 49·1; H, 5·38; Mo, 25·2. Calc. for: $C_{31}H_{41}Mo_2O_{10}$: ($C_{22}H_{32}Mo_2O_{10} + 1{\cdot}5\ C_6H_6$): C, 48·55; H, 5·39; Mo, 25·2%).

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# PREPARATION AND PROPERTIES OF SUBSTITUTED AMMONIUM HEXAFLUOROTITANATES

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**Abstract**—Methods for the preparation of ammonium-type hexafluorotitanates are described. Solubilities, infra-red spectra and X-ray powder diffraction patterns are reported. Thermal decomposition of some of these materials occurs on sublimation and the products obtained are reported. These decomposition products are substituted ammonium fluorides and bifluorides, some of which are not previously described.

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IN the course of a detailed study of the reaction of amines with titanium tetrafluoride, we have had the occasion to prepare for the purpose of comparison with the reaction products a number of ammonium-type hexafluorotitanates. This article deals with the method of preparation, infra-red spectra and X-ray powder diffraction patterns of the hexafluorotitanates. In the attempted sublimation of these materials decomposition occurs and in some instances the compounds produced were identified.

Only a very few ammonium-type hexafluorotitanates have been reported. A number of alkaloids[2] and pyridine[3] are reported to form hexafluorotitanates. It has also been reported that unspecified protonic amines form some hexafluorotitanate when the amine and titanium tetrafluoride are mixed in ether solution.[4] The thermal decomposition of only ammonium hexafluorotitanate has been investigated.[5]

## EXPERIMENTAL

Commercial titanium tetrafluoride (Allied Chemical and Dye Corp.) was used directly. The amines were dried over barium oxide and then fractionally distilled. Acetone was dried over calcium chloride and then fractionally distilled from phosphorus pentoxide.

The infra-red spectra were obtained using a Perkin-Elmer, Model 21, infra-red spectrometer with sodium chloride optics. The instrument was frequency calibrated. X-ray powder diffraction patterns were obtained by the Debye-Scherrer method using copper $K_\alpha$ radiation. Line intensities were estimated visually.

The hexafluorotitanates were prepared in the following manner. Approximately 5 g of titanium tetrafluoride (0·04 moles) was dissolved in 200 ml of acetone. The solution was filtered and then saturated with gaseous hydrogen fluoride. About 0·2 mole of amine was dissolved in 100 ml of acetone and the solution was saturated with hydrogen fluoride. The solutions were mixed and the resulting precipitate was recovered by filtration, washed with acetone and dried in vacuo over calcium chloride.

Thermal decomposition of the hexafluorotitanates was carried out in a vacuum sublimator equipped with a cold finger. The samples were heated for 24–48 hr at 110–140° and the cold finger was at either 20° or −78°, 20° being adequate to trap the condensable material. The hexafluorotitanates were nearly completely volatilized with only a small darkened residue of indefinite composition

(1) (a) Abstracted in part from the Ph.D. thesis, University of Illinois, Urbana, Illinois (1959); (b) ibid. 1961.
(2) J. A. SCHAEFFER, *J. Amer. Chem. Soc.* **30**, 1862 (1908).
(3) H. J. EMELEUS and G. S. RAO, *J. Chem. Soc.* 4245 (1958).
(4) E. L. MUETTERTIES, *J. Amer. Chem. Soc.* **80**, 1082 (1960).
(5) S. HARTMAN, *Z. Anorg. Chem.* **155**, 355 (1926).

remaining. Under these conditions titanium tetrafluoride is not condensed on the cold finger. Under vacuum conditions liquid nitrogen is needed to efficiently trap titanium tetrafluoride vapour.[6]

The hexafluorotitanates were soluble in dimethylformamide, formamide, and dimethylsulphoxide but could not be recovered from these solvents. The di-*n*-propyl-, diisopropyl-, and triethylammonium salts were also soluble but not recoverable in ethanol, benzonitrile and acetonitrile, while they could be recrystallized from chloroform. All were insoluble in other common organic solvents.

## RESULTS

*Ammonium hexafluorotitanate.* This material was prepared according to the reported procedure.[2] Attempted sublimation led to thermal decomposition. The condensable product from thermal decomposition was identified as ammonium fluoride by its X-ray powder diffraction pattern. Found: H, 4·07; N, 14·54; Ti, 24·21. Calc. for $(NH_4)_2TiF_6$: H, 4·04; N, 14·15; Ti, 24·20%. The major X-ray *d* spacings for $(NH_4)_2$ $TiF_6$ with relative intensities in parentheses are: 5·18 (70), 3·52 (70), 2·28 (100), 1·81 (40) and 1·76 (50)

*Di-*n*-propylammonium hexafluorotitanate.* This compound and all subsequent ones were prepared by the method described in the experimental section. Thermal decomposition of this hexafluorotitanate produced a white, hygroscopic sublimate, m.p. 90–92° whose elemental analysis is in agreement with di-*n*-propylammonium fluoride. Found: C, 39·48; H, 8.77; N, 7·60; Ti, 13·7. Calc. for $[(C_3H_7)_2NH_2]_2TiF_6$: C, 39·40; H, 8·80; N 7·65; Ti, 13·1%. The major X-ray *d* spacings of this compound are: 9·19 (75), 7·91 (100), 7·00 (40), 5·56 (30), 5·03 (30), 4·46 (50), 4·17 (80), 3·86 (20) and 3·61 (20). Found: C, 58·5; H, 13·23; N, 11·44. Calc. $(C_3H_7)_2NH_2F$: C, 59·4; H, 13·30; N, 11·55%. The *d* spacings for this fluoride are 12·7 (100), 4·54 (80), 4·11 (100), 3·85 (80), 3·58 (75), 3·35 (30), 3·12 (100), 2·99 (60), 2·67 (10), 2·42 (10), 2·26 (10) and 2·11 (20).

*Diisopropylammonium hexafluorotitanate.* The thermal decomposition of this compound produced a white, very hygroscopic sublimate, m.p. 108–110° which analyzed for diisopropylammonium bifluoride. Found: C, 39·8; H, 8·88; N, 7·58; Ti, 13·3; F, 31·0. Calc. for $[(C_3H_2)_2NH_2]_2TiF_6$; C, 39·4; H, 8·80; N, 7·65, Ti, 13·1; F, 31·0%.

The X-ray *d* spacings are 8·0 (100), 6·71 (30), 5·80 (40), 5·14 (5), 4·17 (80), 3·66 (10) and 3·46 (10). Found: C, 51·4; N, 12·09; N, 9·81. Calc. for $(C_3^iH_7)_2NH_2^+HF_2^-$: C, 51·1; H, 12·10; N, 9·95%. The X-ray *d* spacings of the fluoride are 8·21 (20), 7·04 (100), 5·25 (40), 4·41 (5), 4·11(5) 3·88 (15), 3·22 (10); 2·83 (5) and 2·67 (1).

*Diethylammonium hexafluorotitanate.* No condensable material was obtained by our sublimation procedure. Found: C, 30·3; H, 7·49; N, 8·94. Calc. for $[(C_2H_5)_2$ $NH_2]_2TiF_6$: C, 31.0; H, 7·80; N, 9·05%.

The X-ray *d* spacings are 6·81 (100), 5·58(30), 4·63(10), 4·41 (75), 3·80(50), 3·42(20), 2·86 (5) and 2·46 (1).

*Triethylammonium hexafluorotitanate.* Thermal decomposition of this hexafluorotitanate produced an unstable sublimate which decomposed at room temperature too rapidly to permit analysis. The sublimate did not contain titanium and was probably an unstable triethylammonium fluoride or bifluoride. Found: C, 38·88; H, 8·82; N, 7·35. Calc. for $[(C_2H_5)_3NH]_2TiF_6$: C, 39·40; H, 8·80; N, 7·65%.

The X-ray *d* spacings are 11·7 (5), 8·18 (100), 6·51 (50) 4·31 (70), 3·82 (20), 3·52 (10), 3·07 (5), 2·77 (5) and 2·32 (1).

[6] E. H. HALL, J. M. BLOCHER, JR. and I. E. CAMPBELL, *J. Electrochem. Soc.* **105**, 275 (1958).

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TABLE 1.—INFRA-RED SPECTRA OF HEXAFLUOROTITANATES

| $[(n\text{-}C_3H_7)_2NH_2]_2TiF_6$ | $(n\text{-}C_3H_7)_2NH_2F$ | $[(i\text{-}C_3H_7)_2NH_2]_2TiF_6$ | $(i\text{-}C_3H_7)_2NH_2^+HF_2^-$ | $[(C_2H_5)_2NH_2]_2TiF_6$ | $[(C_2H_5)_3NH]_2TiF_6$ | $[C_5H_5NH]_2TiF_6$ | $[C_4H_8ONH_2]_2TiF_6$ |
|---|---|---|---|---|---|---|---|
| 3021 (*s*) | 2939 (*s*) | 3040 (*s*) | 3040 (*sh*) | 3050 (*s*) | 2876 (*s*) | 3218 (*s*) | 2480 (*s*) |
| 2960 (*s*) | 2865 (*sh*) | 2995 (*sh*) | 2972 (*s*) | 2980 (*s*) | 2692 (*s*) | 3070 (*s*) | 1623 (*m*) |
| 2845 (*s*) | 2691 (*sh*) | 2865 (*sh*) | 2826 (*s*) | 2479 (*m*) | 2496 (*m*) | 2842 (*s*) | 1585 (*m*) |
| 2525 (*m*) | 2505 (*m*) | 2772 (*sh*) | 2702 (*s*) | 2379 (*w*) | 1461 (*s*) | 1703 (*w*) | 1405 (*w*) |
| 2429 (*m*) | 2420 (*m*) | 2496 (*m*) | 2476 (*s*) | 1601 (*s*) | 1401 (*s*) | 1656 (*w*) | 1320 (*sh*) |
| 1616 (*s*) | 1977 (*w*) | 2428 (*w*) | 2418 (*sh*) | 1461 (*s*) | 1375 (*s*) | 1635 (*sh*) | 1318 (*m*) |
| 1591 (*s*) | 1593 (*s*) | 2348 (*w*) | 2327 (*sh*) | 1399 (*sh*) | 1311 (*w*) | 1627 (*sh*) | 1248 (*sh*) |
| 1466 (*s*) | 1476 (*m*) | 2106 (*w*) | 2136 (*s*) | 1385 (*sh*) | 1291 (*w*) | 1611 (*s*) | 1235 (*m*) |
| 1379 (*w*) | 1458 (*s*) | 1598 (*s*) | 1923 (*s*) | 1376 (*s*) | 1165 (*s*) | 1535 (*s*) | 1205 (*w*) |
| 1286 (*w*) | 1406 (*m*) | 1475 (*s*) | 1640 (*s*) | 1310 (*w*) | 1064 (*m*) | 1487 (*s*) | 1180 (*w*) |
| 1271 (*w*) | 1338 (*m*) | 1461 (*sh*) | 1629 (*s*) | 1215 (*w*) | 1034 (*s*) | 1385 (*w*) | 1115 (*s*) |
| 1099 (*m*) | 1210 (*m*) | 1443 (*s*) | 1512 (*s*) | 1168 (*m*) | 889 (*w*) | 1328 (*w*) | 1095 (*s*) |
| 1046 (*s*) | 1094 (*w*) | 1402 (*s*) | 1478 (*s*) | 1068 (*s*) | 850 (*m*) | 1252 (*m*) | 1045 (*s*) |
| 1029 (*m*) | 1044 (*s*) | 1392 (*m*) | 1473 (*s*) | 1047 (*s*) | 803 (*m*) | 1204 (*m*) | 1030 (*sh*) |
| 1009 (*m*) | 1021 (*m*) | 1321 (*m*) | 1398 (*s*) | 803 (*s*) | | 1168 (*w*) | 900 (*w*) |
| 955 (*w*) | 957 (*w*) | 1297 (*w*) | 1382 (*s*) | | | 1074 (*w*) | 873 (*m*) |
| 910 (*w*) | 915 (*w*) | 1202 (*m*) | 1359 (*w*) | | | 1054 (*w*) | 823 (*m*) |
| 840 (*w*) | 847 (*w*) | 1187 (*m*) | 1348 (*w*) | | | 837 (*m*) | 715 (*s,br*) |
| 764 (*s*) | 764 (*s*) | 1170 (*w*) | 1332 (*w*) | | | 759 (*s*) | |
| | | 1152 (*s*) | 1318 (*w*) | | | 675 (*s*) | |
| | | 1100 (*s*) | 1208 (*w*) | | | | |
| | | 947 (*s*) | 1187 (*s*) | | | | |
| | | 830 (*w*) | 1153 (*s*) | | | | |
| | | 805 (*w*) | 1103 (*s*) | | | | |
| | | | 1064 (*s*) | | | | |
| | | | 980 (*m*) | | | | |
| | | | 960 (*w*) | | | | |
| | | | 946 (*w*) | | | | |
| | | | 840 (*w*) | | | | |
| | | | 811 (*s*) | | | | |

*Pyridinium hexafluorotitanate.* Thermal decomposition of this product exhibited behaviour similar to that of triethylammonium hexafluorotitanate. The unstable sublimate is probably pyridinium fluoride or bifluoride. Found: C, 36·1; H, 3·94; N, 8·47. Calc. for $(C_5H_5NH)_2TiF_6$: C, 37·3; H, 3·76; N, 8·69%.

The X-ray *d* spacings are: 8·25 (25), 7·20 (20), 5·01 (100), 4·49 (90), 4·15 (5), 3·42 (10), 3·25 (10), 2·59 (1) and 2·40 (1).

*Morpholinium hexafluorotitanate.* Found: C, 28·04; H, 6·37; N, 8·21. Calc. for $(C_4H_8ONH_2)_2TiF_6$: C, 28·40; H, 5·92; N, 8·28%.

This material is amorphous to X-rays. No thermal decomposition experiments were performed on this compound.

*Piperazinium hexafluorotitanate.* Elemental analysis of this compound indicates that both nitrogens in the piperazine molecule are protonated. Thermal decomposition studies were not performed. (Found: C, 19·77; H, 4·89; N, 11·28. Calc. for $(C_4H_8N_2H_4)TiF_6$: C, 19·13; H, 4·78; N, 11·15%). The X-ray *d* spacings are: 7·85 (60), 5·22 (100), 4·91 (80), 4·20 (80), 3·89 (80), 2·86 (50), 2·59 (50).

*Characteristic infra-red spectra.* The infra-red spectra obtained on these hexafluorotitanates are reported in Table 1 for identification purposes. The spectra are characteristic of the ammonium ion[7] for the hexafluorotitanates have no strong characteristic absorption frequency in this region.

[7] K. NAKANISHI, T. GOTO, M. OHASHI, *Bull. Chem. Soc.* (Japan) **30**, 403 (1957); P. J. STONE, J. C. CRAIG, H. W. THOMPSON, *J. Chem. Soc.* 52, (1958).

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# THE PREPARATION AND PROPERTIES OF *BIS*-DISILANYL SULPHIDE AND *TRIS*-DISILANYLAMINE*

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**Abstract**—The new compounds bis-disilanyl sulphide, $(SiH_3SiH_2)_2S$, and tris-disilanylamine, $(SiH_3SiH_2)_3N$ have been prepared from disilanyl iodide, $SiH_3SiH_2I$ and have been characterized.

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IN a previous paper,[1] the preparation of the first pure disilanyl compounds, $SiH_3SiH_2I$ and $(SiH_3SiH_2)_2O$, was reported. The present communication describes the preparation and properties of two more new compounds of this type—*bis*-disilanyl sulphide and *tris*-disilanylamine. These new compounds are formally the silicon analogs of diethyl sulphide and triethylamine and they form the second members of the homologous series $[SiH_3(SiH_2)_n]_2S$ and $[SiH_3(SiH_2)_n]_3N$. The first members of these series, $(SiH_3)_2S$[2] and $(SiH_3)_3N$[3] have been reported previously.[4]

GAMBOA attempted the preparation of $(SiH_3SiH_2)_3N$ by allowing a mixture of $SiH_3SiH_2Cl$ and $Si_2H_4Cl_2$ to react with $NH_3$, and, although a reaction most certainly occurred, large amounts of polymeric material contaminated with $NH_4Cl$ were formed, from which the desired amine was not recovered.[5]

## EXPERIMENTAL

### *Apparatus*

All work was carried out in a Pyrex glass vacuum system. Stopcocks were lubricated with Apiezon N grease in preference to silicone grease in order to eliminate the possibility of foreign silicon compounds appearing through attack on the grease by the substances handled.

Melting points were determined upon 20–25 mg portions of material by a magnetic plunger technique.[6]

All temperatures below 0° were measured by an iron–constantan thermocouple, standardized by the National Bureau of Standards. Temperatures above 0° were measured with thermometer which had been compared with one standardized by the National Bureau of Standards. In the use of these thermometers, stem corrections were applied where they were significant.

### Bis-*disilanyl sulphide*, $(SiH_3SiH_2)_2S$, *synthesis*.

Freshly distilled disilanyl iodide, 0·697 g, prepared as previously described,[1] vapour-pressure at 0°, 10·5 mm, was passed as a vapour at room temperature through a tube 2 cm × 30 cm packed with alternate layers of glass wool and 30 g of a mixture of pure white sand, 100 g, and red mercuric

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‡ Alfred P. Sloan Research Fellow.

[1] L. G. L. WARD and A. G. MACDIARMID, *J. Amer. Chem. Soc.* **82**, 2151 (1960).
[2] H. J. EMELÉUS, A. G. MACDIARMID and A. G. MADDOCK, *J. Inorg. Nucl. Chem.* **1**, 194 (1955).
[3] A. STOCK and C. SOMIESKI, *Ber. Dtsch. Chem. Ges.* **54**, 740 (1921).
[4] A. G. MACDIARMID, *Quart. Rev.* **10**, 208 (1956).
[5] J. M. GAMBOA, *An. Soc. esp. Fis. Quim.* **46** B, 699 (1950); *Chem. Abstr.* **49**, 6766 (1955).
[6] A. STOCK, *Hydrides of Boron and Silicon*, p. 183, Cornell Univ. Press, Ithaca, New York (1933).

sulphide, 20 g. The volatile materials obtained were condensed in a trap at −196° from which they were later distilled, at room temperature by way of a trap at −46° in which the bulk of the $(SiH_3SiH_2)_2S$, (0·248 g) condensed, yield, 87 per cent. Purification was effected by redistilling the product. Due to its low volatility, molecular weight measurements were performed at 90° by measuring the pressure exerted by a known weight of material when completely vaporized in a given volume, all parts of the apparatus being at 90°. The pure material obtained (mol. wt. found, 155·4, 158·0. Calc. 154·5), exerted a vapour-pressure of 0·5 mm at 0°, and had m.p. −70·4 ± 0·1°; density, 0·950 g/ml at 0°.

*Bis*-disilanyl sulphide did not attack mercury or appear to react with mercury vapour. However, like its lower homologue, $(SiH_3)_2S$ it inflamed spontaneously in air.

*Analysis*. *Bis*-disilanyl sulphide (0·0759 g; 0·491 mmole; vapour-pressure at 0°, 0·5 mm, m.p. −70·0°), upon hydrolysis in 35 per cent aqueous sodium hydroxide, (15 ml), containing ethanol, (2 ml), and piperidine, (2 ml), after warming to approximately 50° upon four occasions, yielded 131·0 ml of hydrogen at s.t.p. (Calc. 132·1 ml). The simultaneous analysis of silicon and sulphur was accomplished by means of the following procedure. The alkaline solution was transferred to a large platinum basin, cooled to 0°, and *without* removing the piperidine or ethanol, 5 ml of liquid bromine was added with stirring. The mixture was kept at 0° for 1 hr and at room temperature for a day and a half. The excess bromine was removed by evaporation and the bromide and bromate were destroyed by repeated evaporations with concentrated nitric acid. The residues were transferred to a porcelain basin and the final traces of organic matter were destroyed with *aqua regia*. The analysis for silicon as $SiO_2$[7] was completed before analysing for sulphate as $BaSO_4$.[8] Si found, 71·7; Calc. 72·72; S found, 21·0; calcd. 20·75%. Another sample, (0·0902 g, vapour-pressure at 0°, 0·5 mm; m.p. −70·0°), yielded hydrogen 156·2 ml at s.t.p. Calc., 157·0 ml., Si found, 72·5; Calc., 72·72%.

*Thermal stability*. (a) No decomposition could be detected after storing a sample of the material at −78° for several weeks. However, the compound underwent partial decomposition after storing at room temperature for one week.

(b) Decomposition at 90°. Evidence of very slight thermal decomposition of the material during molecular weight determinations at 90° during approximately one half hour was obtained by comparing the infra-red spectrum of a sample before and after such a determination. Decomposition was so slight that the vapour-pressure at 0° remained unaltered. The traces of impurity could be removed by redistillation.

(c) Decomposition at higher temperatures. $(SiH_3SiH_2)_2S$, (0·0550 g, vapour-pressure at 0°, 0·5 mm, m.p. −70·4°), was heated from 52·6° to 157·0° during 3 hr over mercury and then cooled to room temperature during a period of 3 hr. The products isolated were $(SiH_3SiH_2)_2S$, (0·0377 g); $Si_2H_6$, (0·0050 g); hydrogen, (0·02 ml) and a white, non-volatile, crystalline residue.

*Vapour pressure*. An immersible tensimeter,* was used in conjunction with compensating manometers at room temperature in order to avoid the necessity of making corrections due to the change in density of mercury with the increase in temperature. The constant temperature bath was controlled to ±0·05°.† Vapour-pressures were observed over the range 0–59·5°, and those pressures in the range 0–34·4° are represented by the equation $\log P_{mm} = \frac{-2487{\cdot}6}{(273{\cdot}16) + t} + 8{\cdot}8494$ (Table 1), computed from data derived during two separate experiments as the temperature increased.

This equation gives an extrapolated boiling point of 144°. The molar heat of vaporization is 11·38 kcal $mole^{-1}$ and Trouton's constant, 27·3 cal $°A^{-1}$ $mole^{-1}$ over the range covered. Deviation of the vapour-pressure curves from linearity at temperatures much above 35° indicates that thermal decomposition was occurring to a measurable extent at the higher temperatures. The poorer agreement between calculated and experimental vapour-pressure values on decreasing the temperature is

* Designed after the one described by BURG and SCHLESINGER,[9] the inner surfaces of which had been thoroughly pre-treated with liquid $(SiH_3SiH_2)_2S$ and its vapour at room temperature during 24 hr.

† Sargent Thermonitor, Model S., E. H. Sargent and Co., Chicago.

[7] A. I. VOGEL, *A Textbook of Quantitative Inorganic Analysis, Theory and Practice*, (2nd Ed.) p. 503. Longmans and Green, London (1951).

[8] A. I. VOGEL, *A Textbook of Quantitative Inorganic Analysis, Theory and Practice*, (2nd Ed.) p. 404. Longmans and Green, London (1951).

[9] A. B. BURG and H. I. SCHLESINGER, *J. Amer. Chem. Soc.* **59**, 780 (1937).

also consistent with slight decomposition at higher temperatures. During the experiments the temperature was increased during a period of approximately 3 hr and decreased during a period of 1 hr.

Tris-*disilanylamine*, $(SiH_3SiH_2)_3N$, *synthesis*.

Freshly distilled pure $SiH_3SiH_2I$, (0·5510 g), contained in a 250 ml vessel, was allowed to react at room temperature in the liquid phase with anhydrous ammonia, (0·0665 g), during one hour, although reaction had commenced at −78°. The volatile products were collected in a trap at −196° from which they were later distilled at room temperature. The almost pure $(SiH_3SiH_2)_3N$ condensed in a trap at −46°, and traces of $NH_3$ and $Si_2H_6$ condensed at −196°. Upon evaporating and recondensing the amine, there remained in the trap at room temperature a small quantity of white, non-volatile product

TABLE 1.—THE VAPOUR-PRESSURE OF *bis*-DISILANYL SULPHIDE*

| Temp.‡ (°C) | Vapour-pressure (mm) | | Temp.‡ (°C) | Vapour-pressure (mm) | |
|---|---|---|---|---|---|
| | Obsd. | Calc. | | Obsd. | Calc. |
| 0·0 | 0·50 | 0·55 | 34·4 | 5·75 | 5·77 |
| 10·0* | 1·25 | 1·16 | 39·6 | 7·60 | 7·87 |
| 11·2* | 1·35 | 1·26 | 44·9 | 10·10 | 10·7 |
| 14·4* | 1·65 | 1·58 | 50·0 | 12·95 | 14·2 |
| 20·1* | 2·45 | 2·33 | 59·5 | 20·85 | 23·5 |
| 24·9* | 3·10 | 3·19 | 50·0 | 13·15† | 14·2 |
| 25·2* | 3·35 | 3·25 | 40·8 | 8·00† | 8·44 |
| 29·3* | 4·20 | 4·22 | 26·3 | 3·55† | 3·49 |
| 29·8* | 4·25 | 4·35 | 11·3 | 1·50† | 1·27 |

* Results of two separate vapour-pressure determinations.
† Pressure observed on decreasing the temperature.
‡ Thermometer was calibrated in tenths of a degree.

which was apparently formed by the decomposition of traces of impurity, possibly primary and secondary disilanylamines. The total weight of product obtained was 0·1244 g; yield, 64 per cent; m.p. −98·0–−96·8°. The trace of impurity was removed by heating the $(SiH_3SiH_2)_3N$ to 90° for several hours in a Pyrex tube, which was then stored at room temperature for several days before opening. Redistillation yielded a pure product which did not deposit a white solid on evaporation. The low volatility of the amine made it necessary to determine its molecular weight at 90°; mol. wt. found, 201·0, 197·8; calc., 197·7; vapour-pressure at 0°, 0·5 mm; m.p. −97·1 ± 0·1°; density, 0·873 g/ml at 0°. Pure $(SiH_3SiH_2)_3N$ is stable when stored in an all Pyrex glass vessel at room temperature. It does not attack mercury, and like its lower homologue, $(SiH_3)_3N$, it is spontaneously inflammable in air.

*Analysis*. *Tris*-disilanylamine, (0·0834 g, vapour-pressure at 0°, 0·6 mm; m.p. −97·0°), upon hydrolysis in 35 per cent aqueous sodium hydroxide, (15 ml), containing ethanol, (2 ml), and piperidine, (2 ml), after warming on three occasions to approximately 50°, yielded 168·3 ml hydrogen at s.t.p., (calc., 170·2 ml). The alkaline hydrolysate was transferred to a large platinum basin from which most of the liquid was evaporated on the steam bath. The analysis for silicon as $SiO_2$ was then completed by a method similar to that used in the analysis of $(SiH_2SiH_2)_2S$. (Found: Si, 85·6. Calc. 85·26%). The analysis for nitrogen was carried out upon a separate sample.§ (Found: N, 6·90. Calc. 7·09%).

*Thermal stability*. $(SiH_3SiH_2)_3N$, (vapour-pressure at 0°, 0·6 mm), was heated to 90° in a Pyrex tube over mercury during 4 hr and then cooled to room temperature. No non-condensable gases were formed, and the vapour-pressure at 0° of the sample at the end of the experiment was 0·6 mm. No change in the vapour pressure of another sample was observed after storage for seventeen days at room temperature in a Pyrex tube. A *very small* amount of a non-condensable gas was formed when the same sample was heated to 150°.

§ Analysis performed by Schwarzkopf Microanalytical Laboratory, 56–19 37th Ave., Woodside 77, New York.



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*Vapour pressure.* The vapour-pressure of the pure, freshly distilled amine was observed over the range 0–150·1° in the apparatus employed for similar experiments with $(SiH_3SiH_2)_2S$, and those pressures in the range 0–121·0° are represented by the equation $\log P_{mm} = \frac{-2328{\cdot}9}{273{\cdot}16 + t} + 8{\cdot}0645$ (Table 2). The extrapolated boiling point is 176°. The molar heat of vaporization is 10·66 kcal mole$^{-1}$ and Trouton's constant, 23·7 cal °A$^{-1}$ mole$^{-1}$. The deviation from linearity of the vapour pressure curve at temperatures above 120° indicates that thermal decomposition was occurring to a measurable extent at the higher temperatures. The temperature was increased during a period of 4 hr and decreased during a period of 1 hr.

TABLE 2.—THE VAPOUR-PRESSURE OF *tris*-DISILANYLAMINE

| Temp. (°C) | Vapour-pressure (mm) | | Temp. (°C) | Vapour-pressure (mm) | |
|---|---|---|---|---|---|
| | Obsd. | Calc. | | Obsd. | Calc. |
| 0·0 | 0·54 | 0·35 | 80·7 | 30·85 | 30·4 |
| 26·2 | 1·95 | 1·93 | 100·1 | 67·05 | 66·9 |
| 42·1 | 4·85 | 4·76 | 110·0 | 96·80 | 96·9 |
| 47·3 | 6·35 | 6·27 | 121·0 | 142·05 | 143 |
| 54·3 | 8·95 | 8·96 | 150·1 | 362·00 | 365 |
| 63·8 | 14·35 | 14·2 | 100·0 | 101·80* | 66·6 |
| 70·0 | 19·10 | 19·0 | 61·4 | 37·80* | 12·7 |
| 73·5 | 22·35 | 22·2 | −196 | 5·0* | 0·0 |

* Pressure observed on decreasing the temperature.

*Infra-red spectra.* Infra-red measurements were made with a Perkin-Elmer 137B Infra-red Spectrophotometer employing a sodium chloride optical system. All measurements were made on the gaseous phase at 25° with the sample confined in a 10 cm cell with 30 mm potassium bromide windows cemented with glyptal resin. $(SiH_3SiH_2)_2S$ was observed at a pressure of 1·4 mm and $(SiH_3SiH_2)_3N$ was observed at a pressure of 1·8 mm. The infra-red spectra of all known disilanyl compounds are given in Table 3; based upon analyses of spectra for silyl compounds the indicated assignments appear to be reasonable. The disilanyl group may be distinguished spectroscopically from the silyl group in analogous compounds by the presence of absorption peaks in the range 760 cm$^{-1}$ to 880 cm$^{-1}$ which are not present in the silyl compounds.[9,10–12]

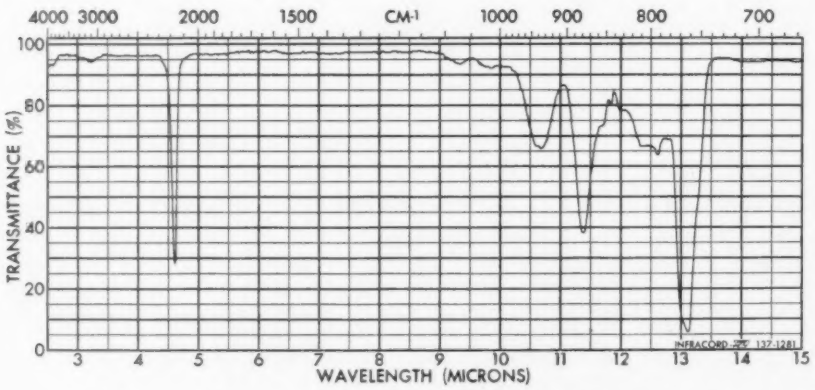


FIG. 1.—Infra-red absorption spectrum of *bis*-disilanyl sulphide, $P_{mm}$. 1·4.

[10] H. R. LINTON and E. R. NIXON, *J. Chem. Phys.* **29,** 921 (1958).
[11] R. C. LORD, D. W. ROBINSON and W. C. SCHUMB, *J. Amer. Chem. Soc.* **78,** 1327 (1956).
[12] D. W. ROBINSON, *J. Amer. Chem. Soc.* **80,** 5924 (1958).

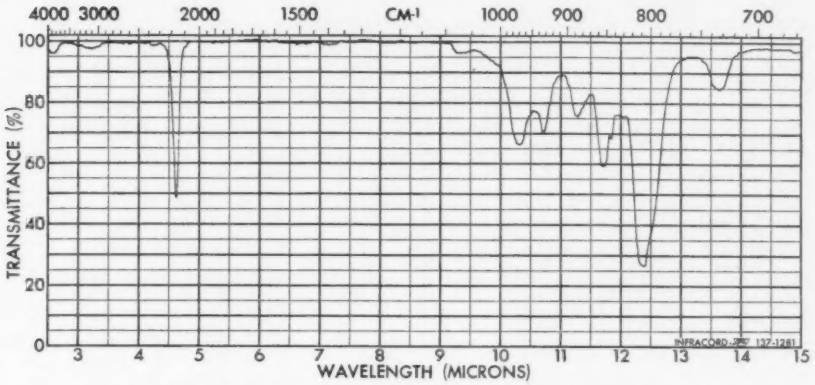


FIG. 2.—Infra-red absorption spectrum of *tris*-disilanylamine, $P_{mm}$. 1·8.

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TABLE 3.—INFRA-RED SPECTRA OF DISILANYL COMPOUNDS

| $Si_2H_5I$[1] | $(Si_2H_5)_2O$ | $(Si_2H_5)_2S$ | $(Si_2H_5)_3N$ | Assignment | Ref. |
|---|---|---|---|---|---|
| 2200 *sh*<br>2180 *s* | 2155 *vs* | 2160 *vs* | 2150 *vs* | Si-H stretch | |
| 1875 *vw*<br>1820 *vw* | | | | Overtone, $SiH_3$ deformation | 13 |
| | 1680 *w* | | | Combn. antisym. and sym. Si-O-Si stretches | 11 |
| 1025 *w* | 1143 *m* | | | | |
| | 1071 *vs* | | | Antisymmetrical Si-O-Si stretch | 11 |
| | | | 968 *s* | Si-N stretch | 12 |
| 944 *m*<br>934 *m*<br>876 *ds*<br>868 *ds*<br>872 *min* | 937 *s*<br><br><br>853 *vs*<br>808 *vs* | 940 *m*<br>878 *s* | 931 *m*<br>885 *m*<br><br>853 *s*<br>845 *m*<br>808 *vs* | Bending of the $SiH_2$ angles in the $SiH_3$ and/or $SiH_2$ groups | 13,14 |
| 761 *dvs*<br>753 *dvs*<br>760 *min* | 755 *m* | 794 *m*<br>764 *vs* | 733 *m* | $SiH_3$ and/or $SiH_2$ rocking | 13 |

[13] H. R. LINTON and E. R. NIXON, *Spectrochim. Acta* **10**, 299 (1958).
[14] H. R. LINTON and E. R. NIXON, *Spectrochim. Acta* **12**, 41 (1958).

*Reaction of* $SiH_3SiH_2I$ *with* $(CH_3)_3N$.

Disilanyl iodide, (0·0737 g, vapour-pressure at 0° found, 10·0 mm; mol. wt. found, 189·5; calc. 188·1), and trimethylamine, (0·0589 g, distilled from barium oxide: mol. wt. found, 58·5; calc. 59·11), were permitted to react during 15 min at room temperature. A nonvolatile white solid was formed. Recovered were disilane, (0·0089 g), silane, (0·0108 g), and trimethylamine, (0·0396 g, mol. wt. found, 59·5; calc., 59·11). The consumption of 0·0193 g of trimethylamine corresponded to the formation of an adduct of composition $SiH_3SiH_2I.[N(CH_3)_3]_{0\cdot83}$.

Since a one-to-one addition compound was not obtained at room temperature, the experiment was repeated at −78°. Very little reaction had taken place after 45 min, and the reactants were therefore permitted to remain at −78° for 48 hr during which period the reaction tube was warmed briefly to room temperature. Of the trimethylamine, (0·1327 g) employed for the reaction, 0·0187 g had been consumed by reaction with 0·0853 g of disilanyl iodide. This corresponded to an adduct of the composition $SiH_3SiH_2I.[N(CH_3)_3]_{0\cdot71}$.

## RESULTS AND DISCUSSION

*Bis*-disilanyl sulphide, $(SiH_3SiH_2)_2S$ has been prepared in yields of 80–90 per cent in a number of experiments by the exothermic reaction at room temperature of the vapour of disilanyl iodide with red mercuric sulphide

$$2SiH_3SiH_2I + HgS \rightarrow (SiH_3SiH_2)_2S + HgI_2 \quad (1)$$

It is spontaneously inflammable in air and it decomposes partly during one week at room temperature. Although decomposition is only just observable after approximately one half hour at 90°, it is more extensive on prolonged heating at temperatures above 50°.

*Tris*-disilanylamine, $(SiH_3SiH_2)_3N$, has been prepared in yields of 58–64 per cent in a number of experiments by the very rapid reaction of stoichiometric quantities of disilanyl iodide and anhydrous ammonia as they warmed from −196° to room temperature.

$$3SiH_3SiH_2I + 4NH_3 \rightarrow (SiH_3SiH_2)_3N + 3NH_4I \quad (2)$$

$(SiH_3SiH_2)_3N$ is spontaneously inflammable in air but it shows the greatest thermal stability of any disilanyl compound so far investigated. No decomposition was detected even on heating to 110°, although slight decomposition was observed above this temperature.

Disilanyl iodide reacts with $N(CH_3)_3$ to produce a white solid of approximate composition $SiH_3SiH_2I.[N(CH_3)_3]_{0\cdot7-0\cdot8}$.

$$SiH_3SiH_2I + N(CH_3)_3 \rightarrow SiH_3SiH_2I.N(CH_3)_3 \quad (3)$$

The compound is apparently less stable than its silyl analogue $SiH_3I.N(CH_3)_3$,[15] and undergoes some complex decomposition during its formation or isolation.

Since silicon falls immediately below carbon in Group IV of the Periodic Table it is of interest to compare the molecular weight and boiling point difference ratios between silyl and disilanyl compounds with those for the analogous carbon compounds.

It should be noted that for comparable structures the degree of intermolecular attraction is less in the silicon compounds than in their carbon analogues since the change in boiling point per molecular weight unit, $\Delta$b.p./$\Delta$mol.wt., is less in the

[15] B. J. AYLETT, H. J. EMELÉUS and A. G. MADDOCK, *J. Inorg. Nucl. Chem.*, **1**, 187 (1955).

TABLE 4.—MOLECULAR WEIGHT AND BOILING POINT DIFFERENCE RATIOS BETWEEN SILYL AND DISILANYL COMPOUNDS AND THEIR CARBON ANALOGUES[16]

| | $\frac{\Delta \text{ b.p.}}{\Delta \text{ mol. wt.}}$ | | $\frac{\Delta \text{ b.p.}}{\Delta \text{ mol. wt.}}$ |
|---|---|---|---|
| $C_2H_5I—CH_3I$ | 2·12 | $Si_2H_5I—SiH_3I$ | 1·90 |
| $(C_2H_5)_2S—(CH_3)_2S$ | 1·92 | $(Si_2H_5)_2S—(SiH_3)_2S$ | 1·41 |
| $(C_2H_5)_2O—(CH_3)_2O$ | 2·07 | $(Si_2H_5)_2O—(SiH_3)_2O$ | 1·83 |
| $(C_2H_5)_3N—(CH_3)_3N$ | 2·04 | $(Si_2H_5)_3N—(SiH_3)_3N$ | 1·38 |

former compounds than in the latter. A similar observation has been made in the case of organosilicon compounds which usually have lower boiling points than the corresponding organic compounds of comparable molecular weight.[17]

*Acknowledgements.* The authors wish to thank Dr. E. R. NIXON for helpful discussions on the interpretation of infra-red spectral data. They also wish to express their appreciation to the Research Corporation for a Frederick Gardner Cottrell Grant which was used to partly support this investigation.

[16] Data obtained from either (a) *Handbook of Chemistry and physics*, (39th Ed.). Chemical Rubber Publishing Company, Cleveland, Ohio (1957), or (b) A. G. MACDIARMID *Quart. Rev.* **10**, 208 (1956).
[17] E. G. ROCHOW, *Chemistry of the Silicones* (2nd Ed.) pp. 110–115. J. Wiley, New York (1951).

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# DECOMPOSITION OF DISILANE–SEPARATION OF SILANE/DISILANE MIXTURES BY GAS PHASE CHROMATOGRAPHY

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**Abstract**—Gas phase chromatography has been used to analyse and separate mixtures of silane and disilane. Chromatographically pure disilane decomposes at a slower rate than impure disilane.

THE purity and stability of higher silicon hydrides have been uncertain because of the limitations of vacuum train techniques and reliable analytical methods. We report in this paper the adaptation of gas chromatography for purifying disilane and for analysing mixtures of silane–disilane. In addition, observations are recorded on the stability of disilane as determined by mass spectrometry.

The separation of silicon hydrides by gas chromatographic techniques has been reported.[1] The present investigation used conventional gas chromatographic analytical equipment for determining the composition of disilane/silane mixtures. Sizeable samples of disilane were purified by large-scale gas chromatography. The relative amounts of silane and disilane were confirmed by mass spectrometric analysis. The chromatographic techniques provided chromatographically pure disilane and a rapid and precise measure of disilane in unknown samples.

The stability of disilane on storage has been reported by GUTOWSKY and STEJSKAL,[2] BETHKE and WILSON,[3] and by WARD.[4] BETHKE and WILSON report no appreciable decomposition of disilane after two months, while GUTOWSKY and STEJSKAL report complete decomposition after eighteen months in Pyrex glass. A sample prepared according to the directions of BETHKE and WILSON but containing a trace of hydrogen iodide was reported to decompose appreciably after seven months[4] We have used mass spectrometric analysis to follow the decomposition of disilane.

## EXPERIMENTAL

Disilane was prepared by the lithium aluminium hydride reduction of hexachlorodisilane by conventional methods.[5] The disilane after purification by trap-to-trap distillation was further purified by fractional distillation through a low-temperature column. However, chlorosilanes were still present as seen by mass spectrometry. The sample (stored in a stainless steel cylinder) was examined periodically by mass spectrometric analysis. The results are tabulated in Table 1.

Gas phase chromatographic analyses were conducted as follows. Samples (approximately 5 mg) were transferred under vacuum to 3 × 150 mm Pyrex glass tubes by gas burette and sealed off while immersed in liquid nitrogen. With a modified air pistol, the glass tube containing the sample was

[1] K. BORER and C. S. G. PHILLIPS, *Proc. Chem. Soc.* 189-190 (1959).
[2] H. S. GUTOWSKY and E. O. STEJSKAL, *J. Chem. Phys.* **22**, 939 (1954).
[3] G. W. BETHKE and M. K. WILSON, *J. Chem. Phys.* **26**, 1107 (1957).
[4] L. G. L. WARD, University of Pennsylvania, Private communication (1960).
[5] A. E. FINHOLT, A. C. BOND, JR., K. E. WILZBACH and H. I. SCHLESINGER, *J. Amer. Chem. Soc.* **69**, 2692–6 (1947).

fired with compressed nitrogen gas into a specially constructed breaking chamber mounted on the Perkin-Elmer model 154-B "Vapour Fracometer". This permitted the rapid, quantitative transfer of the sample for analysis.[6] A two-metre, silica-packed column (Perkin-Elmer "J" column) was used with helium as carrier at a pressure of 20 p.s.i.g. and a flow of 300 ml/min at 75°C. A representative curve illustrating the separation is shown in Fig. 1. The nitrogen peak resulted from the gas used to fire the pistol. The effluent fractions were collected in a series of cold traps and subsequently

TABLE 1.—STABILITY OF DISILANE*

| | Temperature (°C) | $Si_2H_6$† (mole %) | $Si_2H_6$‡ (mole %) |
|---|---|---|---|
| Initial | 30 | 100 | 97·7 |
| | −78 | 100 | — |
| 49 days | 30 | 100 | 93·9 |
| | −78 | 100 | — |
| 154 days | 30 | 97·0 | 84·2 |
| | −78 | 98·5 | — |
| 244 days | 30 | 97·5 | 75·0 |
| | −78 | 98·6 | — |

* Mass Spectrometric Analyses (Consolidated Electrodynamics Corp., Model 21-103-C).
† Purified by gas chromatography.
‡ Purified by trap-to-trap distillation interpolated from plot of concentration *vs.* time. Last analysis showed 54·1 per cent disilane at 423 days.

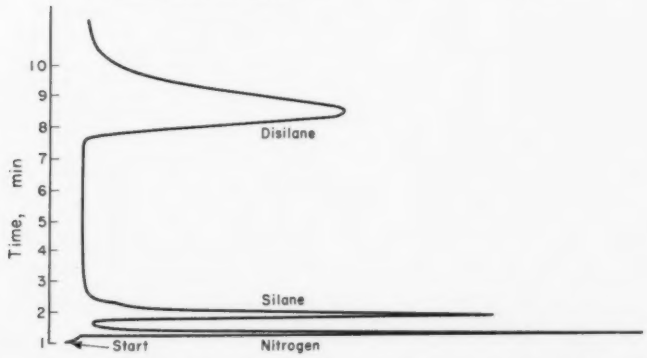


FIG. 1.—Vapour chromatogram. Disilane/Silane mixture Perkin–Elmer "Vapour Fractometer" 154B "J" Column 75°C. 20 p.s.i.g. He.

transferred under vacuum to a Perkin-Elmer "Small Volume Gas Cell", 25 ml volume and 7·5 cm path for infra-red analysis. The infra-red measurements were made with a Perkin-Elmer "Infracord" and Perkin-Elmer Model 21 double beam recording spectrophotometer employing a sodium chloride optical system. The major absorption peaks observed for disilane at 2175 $cm^{-1}$ (very strong), 950 $cm^{-1}$ (strong) and 825–850 $cm^{-1}$ (triplet, very strong), were in accord with literature values.[2] The major absorption peaks at 2050–2300 $cm.^{-1}$ (triplet, very strong), and 910 $cm^{-1}$ (very strong) for silane were also in agreement with published values.[7]

The calculated ratio of disilane/silane from the gas chromatogram was 3·85 (See Table 2) compared to 3·76 from the mass spectrometric analysis. Although the mass spectrometric analysis showed hydrogen as a major impurity, its absence in the chromatographic analysis might be explained by loss during transfer under vacuum. We have not been able to detect chlorosilanes in disilane with these techniques.

[6] J. O. WHITE, Polychemicals Department, E. I. du Pont de Nemours. Unpublished work (1958).
[7] J. W. STRALEY and H. H. NIELSEN, *Phys. Rev.* **62**, 151 (1942).

Gas phase chromatography on a preparative scale was run as follows. A three-gramme sample of disilane of the following purity as determined by mass spectrometry was used.

A 12 ft × 0·75 in. (diam.) copper column, packed with silica gel (DAVISON, 30–60 mesh) and operated at 75°C with a flow of 1500 ml/min of helium, gave a retention of 35·5 min for disilane. Centre cuts of 0·7 g and 0·8 g of disilane were trapped and transferred to 30 ml stainless steel cylinders. These were used for mass spectrometry reference and for decomposition measurements. One sample was stored in solid carbon dioxide and the other at room temperature. After 49 days, both samples showed no decomposition and after 244 days, the compositions were 98·6 and 97·5 per cent respectively.

TABLE 2.—CALCULATION OF RELATIVE AMOUNTS OF SILANE AND DISILANE FROM GAS CHROMATOGRAM

| | Silane | Disilane |
|---|---|---|
| Peak height | 7·01 | 4·41 |
| Width at ½ height | 0·19 | 1·16 |
| Approx. area | 1·33 | 5·12 |
| Mole per cent | 20·6 | 79·4 |
| Ratio (gas chromatography) | 1 | 3·85 |
| Mass Spec. Analysis | 16·2 | 61·0 |
| Ratio (mass spec) | 1 | 3·76 |

| Component | Mole per cent |
|---|---|
| $SiCl_4$ | 0·1 |
| $SiHCl_3$ | 0·1 |
| $SiH_2Cl_2$ | <0·1 |
| $SiH_4$ | 6–7 |
| $Si_2H_6$ | 87–88 |
| $(C_2H_5)_2O$ | 2–3 |
| $H_2O$ | 1–2 |
| $N_2$ and/or air | 1–2 |

## RESULTS AND DISCUSSION

It is readily possible now, by a simple technique using gas chromatography, to determine rapidly and reliably the purity of disilane.

The extension of our analytical techniques to preparatory scale gas chromatography equipment provides an improved method for the purification of silicon hydrides.

We have verified that disilane prepared according to reference (5) decomposes on storage at room temperature. However, disilane purified by gas chromatography showed a slower rate of decomposition. The rate of decomposition, therefore, is influenced by the presence of contaminants. These observations may be significant for chemical investigations requiring pure reagents and for safe handling.

*Acknowledgement*—The mass spectrometric analyses were done by W. M. KIPP, JR. and preparative scale gas chromatography by J. W. ROBSON, both of the Central Research Department.

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# DIVINYLTIN DICHLORIDE DIHYDRATE

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**Abstract**—The preparation of divinyltin dichloride has been reported in two independent publications, which show a discrepancy in melting points of the products.

Our duplication of the reported procedure confirmed one of the two results. An additional product in our preparation was found to be divinyltin dichloride dihydrate. Its preparation, identification and properties are reported.

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Two independent publications for the preparation of divinyltin dichloride by disproportionation of tetravinyltin with tin tetrachloride show different melting points for the final product.[1,2]

Current work in this laboratory made it necessary to prepare this compound and we observed some unexpected phenomena.

Our studies confirmed the lower melting point found by ROSENBERG *et al.*;[2] however, we also obtained a crystalline material from the oily divinyltin dichloride after exposure to moist air.[3]

The identification of this new compound is reported in the following experimental section.

## EXPERIMENTAL

After purified tetravinyltin had been reacted with tin tetrachloride, a large excess of petroleum ether (30–60°) was added and the solution treated with activated charcoal and anhydrous sodium sulphate. After removal of most of the solvent under vacuum, divinyltin dichloride formed a second layer and was separated from the remaining phase. The oil was submitted to reduced pressure (water aspirator) for several hours and allowed to crystallize in a refrigerator. The supernatant solution was cooled to approximately −5° resulting in crystallization of colourless needles. Both fractions were recrystallized from petroleum ether and the melting point of the final product was found to be 14·8–15·0°. (Found: C, 20·1, 19·9; H, 2·4, 2·4%. Calc. for $C_4H_6Cl_2Sn$: C, 19·71, H, 2·48%). Upon filtration at room temperature, these crystals melted to an oil and simultaneously reacted with condensed moisture from the air, which caused the oil to solidify. This solid crystalline product is generally formed when divinyltin dichloride is exposed to moist air or recrystallized from water or alcohol.

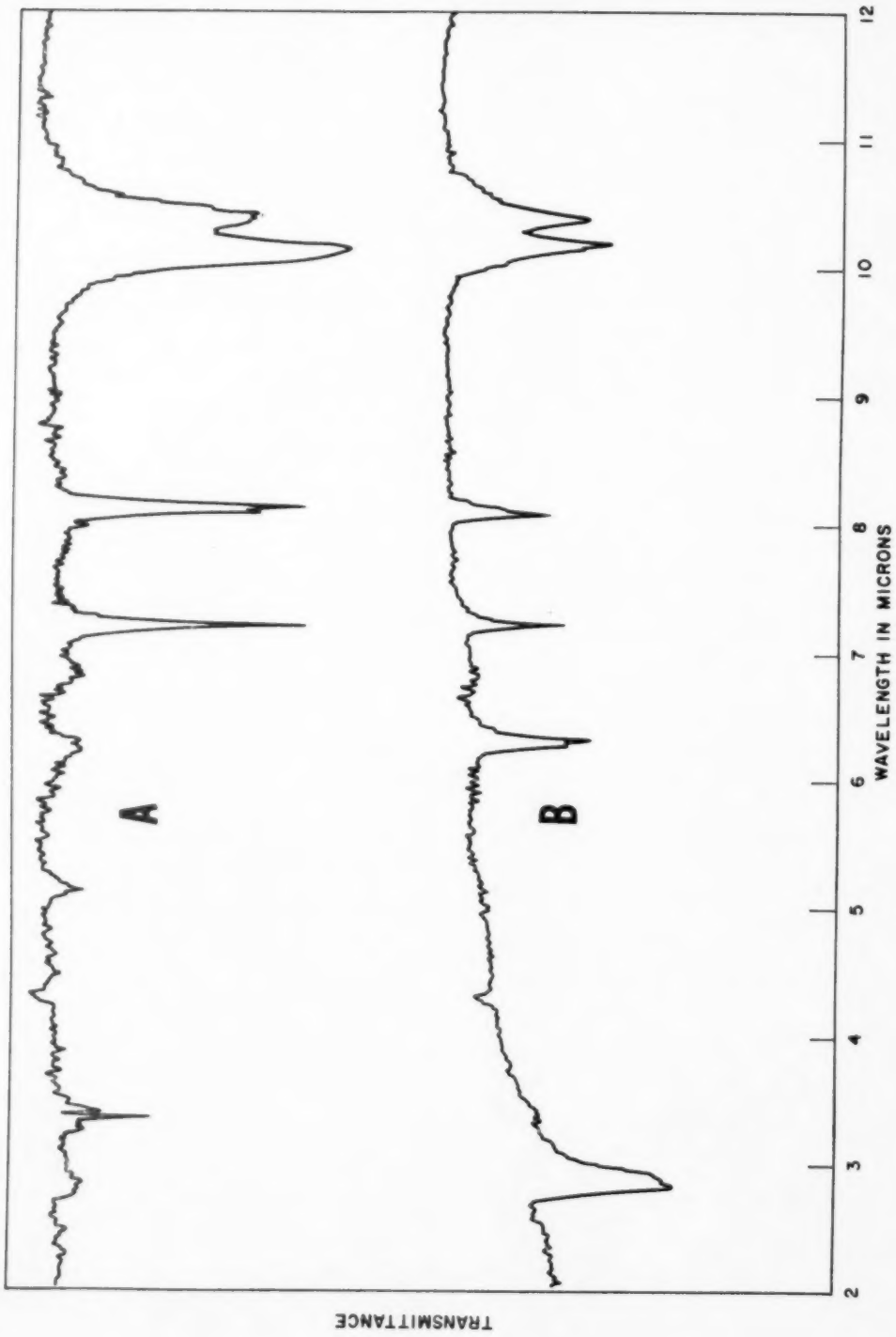
The highest melting point was found to be 43° (sharp).

In dry air, especially in presence of drying agents, such as silica gel, the oily divinyltin dichloride is reformed. (Found: C, 20·1, 20·0; H, 2·5, 2·4% m.p. 14·8–15·0°). The weight loss based on the crystalline material was found to be 12·74 per cent.

The crystalline compound is obtained as prismatic needles or tablets presumably monoclinic or distorted orthorhombic. It is extremely soluble in water, alcohol and acetone, slightly soluble in chloroform and practically insoluble in nonpolar solvents such as carbon tetrachloride and benzene.

Except for two additional bands of 2·9 and 6·3 $\mu$ for the crystalline compound, the infra-red absorption spectra are the same for both oily (*A*) and crystalline material (*B*). Small shifts in some

(1) D. SEYFERTH and F. G. A. STONE, *J. Amer. Chem. Soc.* **79**, 517 (1957).
(2) S. D. ROSENBERG and A. J. GIBBONS, JR., *J. Amer. Chem. Soc.* **79**, 2139 (1957).
(3) In private communications, SEYFERTH explains the higher melting point as preferential crystallization of $Et_2SnCl_2$ and/or $EtViSnCl_2$ impurities formed from the ethyl bromide found to be an impurity in the starting vinyl bromide.


A
B
2
3
4
5
6
7
8
9
10
11
12
WAVELENGTH IN MICRONS
TRANSMITTANCE

bands and different intensities in others are most likely due to the different physical states of the two compounds.

The determination of all elements except oxygen was carried out by Schwarzkopf Microanalytical Laboratory, Woodside 77, New York. (Found: C, 17·41; H, 3·32; Cl, 25·43; O, 10·96*; Sn, 42·88. Calc. for $C_4H_6Cl_2Sn{\cdot}2H_2O$: C, 17·18; H, 3·60; Cl, 25·35; O, 11·44; Sn, 42·43%).

## DISCUSSION

The two bands at about 2·9 and 6·3 $\mu$ in the spectrum of *B* indicated that the crystalline material is a hydrate of the oily anhydrous divinyltin dichloride. This assumption could be confirmed by analytical data. Although the percentages found for carbon, chlorine and tin are high (which could be due to loss of water between preparation and analysis), the calculated formula is still closer to the dihydrate than to a possible dimer or 1·5 hydrate. The observed weight loss of 12·74 per cent on drying the crystalline compound also corresponds to the calculated loss of 12·88 for the dihydrate.

Tin tetrachloride also shows an increased melting point for the pentahydrate; however, a decrease is reported[4] when diethyltin dichloride is hydrated.†

No explanation can be given why other dialkyl or diaryltin dichlorides have not been found to form dihydrates, as it seems probable that the two molecules of water are used to satisfy the coordination number of six for the tetravalent tin in divinyltin dichloride dihydrate.

* By difference.

† The melting point reported by SEYFERTH and STONE coincides with that of the hydrate of diethyltin dichloride, reported by PFEIFFER.

[4] P. PFEIFFER, *Ber. Dtsch. Chem. Ges.* **35**, 3306 (1902).

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# THE PREPARATION AND PROPERTIES OF SOME *CIS* AND *TRANS* RING SUBSTITUTED DIBENZOATO *BIS*(ETHYLENEDIAMINE) COBALT(III) IONS*

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(*Received* 16 *March* 1961)

**Abstract**—Eight *m*- and *p*-substituted complexes of the series *cis*-$[Coen_2(OCOC_6H_4X)_2]ClO_4$ and their corresponding *trans* isomers have been prepared and characterized by their absorption spectra. The *cis* isomers were obtained by the reaction of *cis*-$[Coen_2Cl_2]ClO_4$ with the appropriate silver benzoate at room temperature, whereas the *trans* isomers resulted from the thermal isomerization of the *cis* complexes in methanol solution. The reaction of *trans*-$[Coen_2Cl_2]ClO_4$ with silver benzoate at room temperature yielded mainly a *cis* product. The *m*-nitrobenzoate salts were also obtained for the *m*-nitro substituted complex ions. The ultra-violet and visible spectra of the complexes were found to be similar to those of Linhard's $[Coen_2(OCOCH_3)_2]ClO_4$ especially with respect to the visible absorption, where the two isomers can be differentiated by a split band in the 500 m$\mu$ region.

IN connexion with reactivity studies in co-ordination chemistry, a programme was recently started in this Laboratory to synthesize octahedral complexes of familiar types containing aromatic carboxylato groups, $ArCOO^-$, as the acido ligands. The synthesis of the complex ion $[Co(NH_3)_5OCOC_6H_5]^{2+}$ has been reported elsewhere[1] and extended to other members of the series $[Co(NH_3)_5OCOAr]^{2+}$.[2] We now report the synthesis of another type of complex ions, i.e., $[Coen_2(OCOAr)_2]^+$. As the acido ligands, eight benzoato groups were considered in each of the two possible series, *cis* and *trans*, including the following substituents in the aromatic ring: H, *p*-$CH_3O$, *m*- and *p*-$CH_3$, *m*- and *p*-Cl, *m*-F and *m*-$NO_2$. These groups were selected in order to cover a broad range of electronic effects in view of the subsequent studies.

*Synthetic methods.* The benzoato pentammino cobalt(III) ion can be obtained by reaction of silver benzoate with the chloro pentammino cobalt(III) ion. This reaction has now been applied to dichloro *bis*(ethylenediammine) cobalt(III) ions with a number of *m*- and *p*-substituted silver benzoates. The scope of the reaction appeared to be general for the synthesis of the *cis*-dibenzoato complexes from *cis*-$[Coen_2Cl_2]^+$ with all the substituents investigated in this study. When the reactants are suspended finely powdered in methanol, the reaction proceeds practically to completion in a few hours at room temperature. In the presence of sufficient amounts of alcohol, the complex product dissolves in the diluent and colour changes in the mixture are a useful indication for the detection of the end of the reaction (see Experimental). Although an accelerating factor, heating is to be avoided as it promotes isomerization.

* Structure and Reactivity in Octahedral Complexes—I
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[1] G. ILLUMINATI, *Rend. Acc. Naz. Lincei.* (VIII), **24**, 158 (1958).
[2] Unpublished studies.

The reaction of the *trans*-$[Coen_2Cl_2]^+$ ion with silver benzoates appeared to follow a different course as it occurs with change to the *cis* configuration when it is run at room temperature. At higher temperature, i.e., at 65–75°, the *trans* isomer results, probably through an isomerization subsequent to the primary *cis* product. *Cis* to *trans* thermal isomerization in methanol, which has been studied recently[3] in similar complexes, was now proved for *cis*-$[Coen_2(OCOC_6H_4X)_2]^+$ ions as a general reaction for this series. Thus, it was applied to the synthesis of the *trans* isomers by using the *cis*-$[Coen_2(OCOC_6H_4X)_2]^+$ ions, prepared as described above, as starting materials. With the aid of a preliminary rate examination of the reaction based on spectral changes, the *cis* complexes were found to isomerize practically completely when kept at 60°C for a few days in methanol solution. The moderate solubility of the complexes in this solvent was sufficiently high to lend the method a synthetic significance.

The complexes can be obtained as perchlorates or nitrates by using the corresponding salts of the starting complex ions. The complex *cis*-$[Coen_2(OCOC_6H_4NO_2)_2]$-$OCOC_6H_4NO_2$ was obtained from *cis*-$[Coen_2Cl_2]Cl$ by displacing all three chlorine atoms with silver *m*-nitrobenzoate. The *trans m*-nitrobenzoate salt was then prepared by isomerization of the *cis* form in the usual manner.

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Purified samples were obtained by washing the products with appropriate solvents as recrystallization was not a convenient purification method. They were generally analyzed for cobalt by an electrolytic method.[4] The results were confirmed by analyses for $ClO_4^-$ ion whenever such a check was run.

*Spectral characterization.* The structure of the *cis* and *trans*-isomers described in the preceding section was assigned on the base of their spectral behaviour. The spectra were recorded in the region of 220 to 580 m$\mu$ usually in methanol solution. In the case of the less soluble *trans*-$[Coen_2(OCOC_6H_4NO_2)_2]ClO_4$ and *trans*-$[Coen_2$-$(OCOC_6H_4NO_2)_2]OCOC_6H_4NO_2$, methanol could be replaced by 80 per cent aqueous acetone or 80 per cent aqueous methanol since the solvent effect on the spectra with respect to methanol was found to be small or negligible by comparing the spectra of *cis* and *trans*-$[Coen_2(OCOC_6H_5)_2]ClO_4$ in the three media. The data are collected in Table 1.

First of all, it may be noted from Fig. 1 that in the visible region the spectra of the complexes under examination are closely similar to the corresponding complexes containing aliphatic carboxylato groups as the acido ligands.[5] More generally, the spectra appear to be in accord with the behaviour observed for complex ions of the type $CoA_4B_2$[6,7] and predicted from crystal field theory.[6,8] Thus, due to the nature of the ligands ($A_4 = en_2$ and B = OCOR), the *trans* isomers show a pronounced splitting of band I with a long wavelength component (I*a*) more intense than the short wavelength component (I*b*) and a total area under the split bands smaller than that for band I in the *cis* isomers (Fig. 2). Band I was therefore used to distinguish between *cis* and *trans* forms. Data from the split band I*b* were not included in Table 1 because the band generally appears as a shoulder at 450–460 m$\mu$ with log $\varepsilon$ values of about 1·5.

[3] D. D. Brown and R. S. Nyholm, *J. Chem. Soc.* 2696 (1953; R. C. Brasted and C. Hirayama, *J. Amer. Chem. Soc.* **80,** 788 (1958).
[4] V. M. Linhard and G. Stirn, *Z. Anorg. Chem.* **268,** 105 (1952).
[5] V. M. Linhard and M. Weigel, *Z. Anorg. Chem.* **264,** 321 (1951).
[6] F. Basolo, C. J. Ballhausen and J. Bjerrum *Acta Chem. Scand.* **9,** 810 (1955).
[7] V. M. Linhard and M. Weigel, *Z. Anorg. Chem.* **271,** 101 (1952).
[8] L. E. Orgel, *J. Chem. Phys.* **23,** 1004 (1955).

In the second place the visible absorption, which is associated with transitions within the *d*-shell of the ion[9] is essentially independent of the structure of the aromatic acido ligand. This may appear obvious, since the complex ions belong to the same type of Linhard's ions $[Coen_2(OCOR)_2]^+$; however, it seems of interest to note that the electronic structure of R for the benzoato ligands examined in this work is markedly affected by such substituents as $CH_3O$ and $NO_2$.

TABLE 1.—SPECTRAL DATA FOR SOME *cis* AND *trans*-$[Coen_2(OCOC_6H_4X)_2]^+$ IONS*

| X | | Observed bands for the *cis* isomers | | | Observed bands for the *trans* isomers | | |
|---|---|---|---|---|---|---|---|
| | | I | II** | III | I*a* | II** | III |
| *H*† | $\lambda_{max}(m\mu)$ | 507 | 365 | 231 | 541 | 360 | 239 |
| | $\log \varepsilon_{max}$ | 2·23 | 2·10 | 4·82 | 1·87 | 1·96 | 4·73 |
| *p*-$CH_3O$ | $\lambda_{max}$ | 507 | *s* | 251 | 544 | *s* | 259 |
| | $\log \varepsilon_{max}$ | 2·25 | | 4·65 | 1·95 | | 4·69 |
| *p*-$CH_3$ | $\lambda_{max}$ | 507 | 363 | 238 | 543 | *s* | 247 |
| | $\log \varepsilon_{max}$ | 2·20 | 2·12 | 4·65 | 1·92 | | 4·66 |
| *m*-$CH_3$ | $\lambda_{max}$ | 508 | 365 | 235 | 542 | 360 | 243 |
| | $\log \varepsilon_{max}$ | 2·20 | 2·10 | 4·62 | 1·91 | 1·99 | 4·63 |
| *p*-Cl | $\lambda_{max}$ | 508 | 366 | 239 | 543 | 359 | 246 |
| | $\log \varepsilon_{max}$ | 2·18 | 2·10 | 4·71 | 1·91 | 2·00 | 4·74 |
| *m*-Cl | $\lambda_{max}$ | 510 | 365 | 234 | 547 | 359 | 239 |
| | $\log \varepsilon_{max}$ | 2·18 | 2·09 | 4·59 | 1·89 | 1·97 | 4·60 |
| *m*-F | $\lambda_{max}$ | 506 | 365 | 231 | 543 | 360 | 237 |
| | $\log \varepsilon_{max}$ | 2·18 | 2·09 | 4·61 | 1·88 | 1·96 | 4·73 |
| *m*-$NO_2$‡ | $\lambda_{max}$ | 504 | *s* | — | 542 | — | — |
| | $\log \varepsilon_{max}$ | 2·18 | | — | 1·86 | — | — |

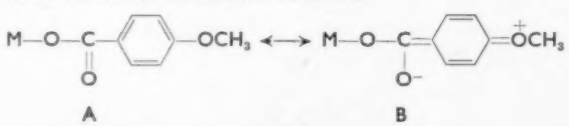
* All complexes examined as perchlorates in methanol solution except when otherwise indicated.

† The data for the unsubstituted term of the series in water solution are as follows: *cis*-isomer, $\lambda_{max}(\log \varepsilon)$, 505 (2·19), 362 (2·08), 227 (4·60); *trans* isomer, 546 (1·91), 358 (1·99), 240 (4·59).

‡ The data entered in the Table for the *trans* isomer refer to measurements in 80 per cent aq. acetone solution. The data for both *m*-nitro complex ions as *m*-nitrobenzoate salts in methanol solution are as follows: *cis*, 506 (2·14); *trans*, 545 (1·93); the other peaks appear as shoulders.

** *s* = shoulder.

Finally, the high band III in the ultra-violet region (Fig. 1), which has been attributed to absorption of the carboxylato group,[5] in our case involves absorption of the aromatic ring as well and, also, interaction between the two (directly linked) groups. Thus, the 20 m$\mu$ bathochromic shift found for *p*-$CH_3O$ is probably associated with resonance interaction between structures A and B




A B

The general bathochromic shift of this band as compared with the complexes containing acetato ligands and the increased breadth found for some of the substituents is in some cases responsible for extensive overlapping with band II. The

[9] F. BASOLO and R. G. PEARSON, *Mechanisms of Inorganic Reactions*, p. 368. J. Wiley, New York (1958).

effect of a *p*-$CH_3O$ group is shown in Fig. 1. No essential differences were observed for band III between *cis* and *trans* complexes except for a slight bathochromic shift in the latter complexes.

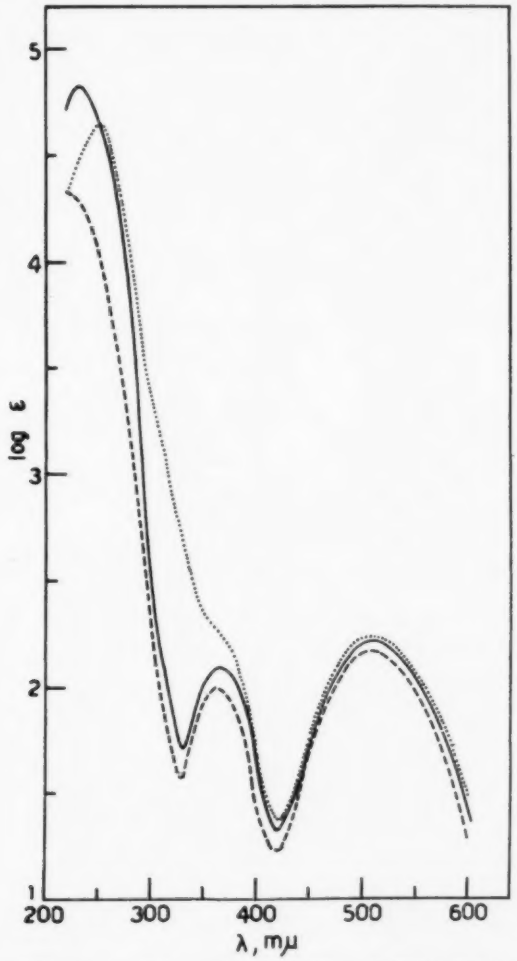



FIG. 1.—Absorption spectra of the complexes *cis*-$(Coen_2(OCOR)_2)ClO_4$ in methanol solution R = $CH_3$ (dashed line), $C_6H_5$ (solid line), *p*-$C_6H_4$-$OCH_3$ (dotted line).

*Other properties.* All dibenzoato complexes herein described melt with decomposition in the range of 210–240°C. The *cis* isomers are usually obtained as pink-violet crystalline powders; their solutions in either water or alcohol are red and red-violet, respectively. Solubility in such solvents is rather poor ($10^{-2}$ to $10^{-1}$ mole/l.), but the *cis* isomers are distinctly more soluble than the *trans* isomers and methanol is a better solvent than ethanol and water. The *trans*-di(*m*-nitrobenzoato) complex is the least soluble of all compounds examined; however, 80 per cent aqueous acetone dissolved appreciable amounts of this ion (ab. $10^{-3}$ mole/l.) and the *m*-nitrobenzoate

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salt proved to be more soluble than either the perchlorate or the nitrate in such a solvent.

Spectral evidence shows that aqueous solutions of the *cis* unsubstituted dibenzoato complex are slightly decomposed in 5 hr. time at 25°C whereas the *trans* isomer remains unchanged under the same conditions. Complexes of either type are smoothly cleaved by alkalis into the dihydroxo *bis*(ethylenediamine)cobalt(III) ion and the corresponding benzoic acid. The latter reaction is studied in detail in the following paper.

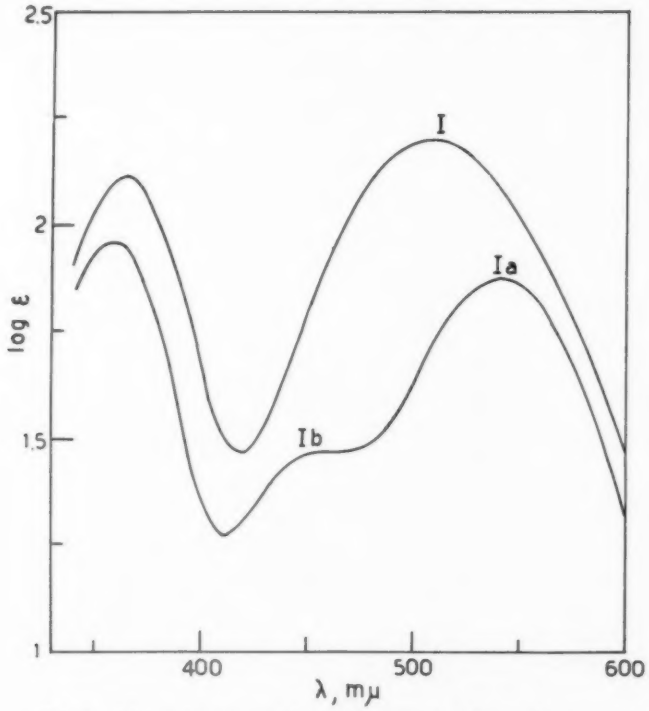


FIG. 2.—Absorption spectra of *cis* (higher curve) and *trans* (lower curve) $(Coen_2(OCOC_6H_5)_2]\ ClO_4$ in methanol solution.

## EXPERIMENTAL

*Materials.* Silver benzoates were prepared by reaction of the corresponding benzoic acid with silver nitrate in the presence of sodium carbonate in water according to available methods.[10] The starting benzoic acids were purified by recrystallization of the commercial samples when necessary. *Trans*-$[Coen_2Cl_2]Cl$ and $[Coen_2Cl_2]ClO_4$ were essentially prepared according to the directions reported by LINHARD and STIRN for the latter salt. *Cis*-$[Coen_2Cl_2]Cl$ was prepared as described by BAILAR[11] and the corresponding perchlorate by precipitation from a solution of the chloride on addition of a sodium perchlorate solution. Both *cis* and *trans*-$[Coen_2(OCOCH_3)_2]ClO_4$ were obtained by LINHARD and STIRN's method.[4] All these starting complexes were analysed for cobalt as a general purity test.

Commercial absolute alcohols were used throughout the work. Use of "super-dry" ethyl alcohol did not prove to be essential in any of the following experiments. All chemicals not specifically mentioned in this section were reagent-grade.

[10] A. A. NOYES and D. SCHWARTS, *J. Amer. Chem. Soc.* **20**, 742 (1898); F. EPHRAIN and A. PFISTER, *Helv. Chim. Acta* **8**, 369 (1925).

[11] J. C. BAILAR, JR., *Inorganic Syntheses* Vol. 2, p. 222. McGraw-Hill, New York, (1946).

Cis-*dibenzoato* bis(*ethylenediamine*) *cobalt*(III) *perchlorates*. A finely powdered mixture of 5·22 g of *cis*-[$Coen_2Cl_2$]$ClO_4$ (0·015 mole) and 0·030 mole of a *m*- or *p*-substituted silver benzoate together with 250–350 ml of methyl alcohol were placed in a 500 ml ground-glass three-necked flask. The mixture was protected from moisture with a $CaCl_2$ tube and from the daylight by wrapping the flask with a black cloth. It was then stirred vigorously at room temperature for a day or so until the solution became deep red and the violet colour of the starting material disappeared from the white silver chloride residue. The reaction mixture was filtered through a sufficiently high-mesh sintered glass crucible to yield a clear solution and the residue washed with small portions of methyl alcohol until a nearly colourless filtrate was obtained. The combined filtrate was evaporated on a water bath kept at 40°C and the concentrated solution was filtered if necessary. The remaining solvent was finally removed by slow evaporation on the slightly warm roof of an oven. The residue, if crystalline, was washed with absolute ethyl alcohol and ether and stored in a vacuum desiccator. In a number of cases, however, the evaporation residue was obtained in the form of a thick and sticky syrup. There was found no general rule to resolve such a material into a solid product, but at least one of the following operations was found effective in doing so, i.e., recrystallization from a concentrated ethanol solution induced by robbing the walls of the flask, precipitation from a concentrated ethanol solution by addition of ether, prolonged grinding of the material under ether or a saturated $NaClO_4$ aqueous solution and, finally, prolonged drying in an Abderhalden apparatus over $CaCl_2$. In the case of the *m*- and *p*-ditoluato complexes the latter procedure was found essential in removing traces of solvent and yielding correct analyses.

The yields and the analytical data of the complexes of this series are reported in Table 2.

Cis-*di*(m-*nitrobenzoato*)bis(*ethylenediamine*)*cobalt*(III) m-*nitrobenzoate*. A mixture of 4·54 g of *cis*-[$Coen_2Cl_2$]Cl (0·0161 mole) and of 13·2 g of silver *m*-nitrobenzoate (0·0483 mole) in 350 ml of methanol was made to react according to the above general procedure. The product was obtained as a crystalline solid, washed with absolute ethanol and ether and finally dried in a vacuum desiccator. It gave a negative Beilstein test for halogens. Yield: 47 per cent. (Found: Co, 8·96. Calc. for [$Coen_2(OCOC_6H_4NO_2)_2$]$OCOC_6H_4NO_2$: Co, 8·70%)

*The reaction of* trans-[$Coen_2Cl_2$]$ClO_4$ *with silver benzoates*. A mixture of 2·50 g of *trans*-[$Coen_2Cl_2$]-$ClO_4$ (0·00715 mole) and of 3·28 g of silver benzoate (0·0143 mole) in 250 ml of methyl alcohol was made to react at room temperature under the same conditions of the reaction of *cis*-[$Coen_2Cl_2$]$ClO_4$ as described above. The reaction of the *trans* isomer appeared to proceed more sluggishly and, after one day, appreciable amounts of unreacted green complex were still left out in the residue. The products were nevertheless isolated from the deep red methanol solution in the usual manner and obtained as 0·75 g of red powder. Yield: 20 per cent. (Found: Co, 11·22. Calc. for $Coen_2(OCOC_6H_5)_2$-$ClO_4$: Co, 11·32%).

On running the absorption spectrum in the visible region and comparing the data (log $\varepsilon$, 2·19 and 2·09 at 510 and 364 m$\mu$, respectively, with no splitting of the first band) with those of *cis* and *trans*-[$Coen_2(OCOC_6H_5)_2$]$ClO_4$ (Table 1 and Fig. 2) this product was found to be largely consisting of the *cis* isomer.

Analogous results were obtained in the reaction with silver *m*-nitrobenzoate, *cis*-[$Coen_2(OCOC_6$-$H_4NO_2)_2$]$ClO_4$ being the product also in this case.

In another experiment, the reaction of *trans*-[$Coen_2Cl_2$]$ClO_4$ with silver benzoate was carried out at higher temperature by heating the mixture in absolute ethanol at 65–75°C for about 20 hr. The product formed in this way proved to be essentially *trans*-[$Coen_2(OCOC_6H_5)_2$]$ClO_4$ by spectral identification. Yield: 72 per cent. (Found: Co, 11·32. Calc. for [$Coen_2(OCOC_6H_5)_2$]$ClO_4$: Co, 11·32%)

Trans-*dibenzoato* bis(*ethylenediamine*)*cobalt*(III) *perchlorates*. A $2·8–3·7 \times 10^{-3}$ M solution of a *cis*-[$Coen_2(OCOC_6H_4X)_2$]$ClO_4$ in absolute methanol was heated at 60°C in a ground-glass 2-necked flask provided with a condenser and protected from moisture with a $CaCl_2$ tube and from daylight with a black cloth. Samples were withdrawn for spectral examination at convenient time intervals (usually once a day) and the corresponding spectra recorded in the 330–600 m$\mu$ region. The reaction was stopped when the peak of the *trans* isomer at 545 m$\mu$ reached a log $\varepsilon$ value of about 1·9. This usually required 70–80 hr. To recover the product, the solution was evaporated in porcelain dish to small volume by cautious heating on a hot plate. On cooling, the red crystalline product obtained was transferred into a sintered glass crucible, washed with several small portions of water until the colour of the filtrate turned from orange-red to violet-red, then with little absolute ethyl alcohol and



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dry ether and finally dried in a vacuum desiccator. The yields and the analytical data for each individual compound are reported in Table 2.

Trans-*di m-nitrobenzoato* bis(*ethylenediamine*)*cobalt*(III)m-*nitrobenzoate*. This complex was prepared according to the preceding general procedure by using *cis*-$[Coen_2(OCOC_6H_4NO_2)_2]OCOC_6H_4NO_2$ as starting material. Yield: 87 per cent. (Found: Co, 9·01. Calc. for $[Coen_2(OCOC_6H_4NO_2)_2]OCOC_6H_4NO_2$: Co, 8·70.)

TABLE 2.—YIELDS AND ANALYTICAL DATA FOR THE PREPARATION OF THE COMPLEXES $[Coen_2(OCOC_6H_4X)_2]ClO_4$

| X | Yield (%) | Co analysis (%) | | $ClO_4^-$ analysis (%) | |
|---|---|---|---|---|---|
| | | Calcd. | Found | Calcd. | Found |
| *Cis* Isomers | | | | | |
| H | 78 | 11·32 | 11·46 | 19·10 | 19·40 |
| *p*-$CH_3O$ | 50 | 10·15 | 10·16 | | |
| *p*-$CH_3$ | 88 | 10·73 | 10·74 | | |
| *m*-$CH_3$ | 74 | 10·73 | 10·95 | | |
| *p*-Cl | 89 | 9·99 | 10·12 | 16·87 | 16·50 |
| *m*-Cl | 38 | 9·99 | 10·05 | | |
| *m*-F | 32 | 10·55 | 10·34 | | |
| *m*-$NO_2$ | 54 | 9·65 | 9·64 | | |
| *Trans* Isomers | | | | | |
| H | 93 | 11·32 | 11·46 | 19·10 | 19·20 |
| *p*-$CH_3O$ | 72 | 10·15 | 10·26 | | |
| *p*-$CH_3$ | 92 | 10·73 | 10·71 | | |
| *m*-$CH_3$ | 91 | 10·73 | 10·59 | | |
| *p*-Cl | 89 | 9·99 | 9·67 | | |
| *m*-Cl | 68 | 9·99 | 10·04 | | |
| *m*-F | 60 | 10·55 | 10·50 | | |
| *m*-$NO_2$ | 90 | 9·65 | 9·34 | | |

*Spectrophotometric measurements*. Visible and ultra-violet absorption spectra were obtained with a Beckman model D.U. quartz spectrophotometer at room temperature. Solutions of the complexes were about $3·5 \times 10^{-3}$ M for the visible region and $2 \times 10^{-5}$ M for the ultra-violet region. The optical densities of such solutions were measured in 10-mm ground-glass stoppered silica cells for all complexes except for *trans*-$[Coen_2(OCOC_6H_4NO_2)_2]ClO_4$, the low solubility of which required the use of 40-mm cells. Lambert-Beer law was tested in the case of *cis* and *trans*-$[Coen_2(OCOC_6H_5)_2]ClO_4$ in water and in methanol solution and found to be obeyed in a satisfactory manner.

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# REDUCTION OF RHENIUM(VII) AT THE DROPPING MERCURY ELECTRODE

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(*Received* 13 *March* 1961)

**Abstract**—The reduction of rhenium(VII), potassium perrhenate, at the dropping mercury electrode has been studied in sodium perchlorate, potassium oxalate, potassium iodide, potassium thiocyanate and potassium cyanide media. In the first four cases reduction begins at ca. −1·4 V vs. the saturated calomel electrode, but the limiting current in each case is even higher than that expected for the change from Re(VII) to Re(−I) and the waves appear to be catalytic in nature. In a cyanide medium (0·5 to at least 2 M potassium cyanide) a well-defined wave is obtained which appears to be diffusion-controlled, involving the reduction of Re(VII) to Re(O). In this medium the limiting current (diffusion current) is proportional to the concentration of rhenium(VII) from 0·3 to at least 2 mM. Evidence has also been obtained as to the existence in solution of a cyano complex of rhenium(O).

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RHENIUM exhibits variable valency and offers an interesting field for investigation by polarographic methods. In acetate[1] and phosphate[2] buffers rhenium(VII) is known to give rise to catalytic waves. However, in hydrochloric and perchloric acid media at suitable concentrations rhenium(VII) gives clean well-defined waves which appear to result from the reduction of Re(VII) to Re(IV)[3]. Recently COLTON *et al.*[4] have investigated the polarographic reduction of rhenium(VII) in a variety of supporting electrolytes in aqueous solution. In an attempt to obtain more information on the lower oxidation states of rhenium, and with a view to establishing a convenient rapid method for the determination of rhenium, the investigations reported here were undertaken.

## EXPERIMENTAL

**Reagents.** All chemicals were of reagent grade and double-distilled water was used throughout for making the solutions.

*Polarographic measurements.* Polarograms were recorded using a Cambridge Pen-recording Polarograph with a dropping mercury electrode (D.M.E.) and an external saturated calomel reference electrode (S.C.E.). The solutions were maintained at 25 ± 0·1°C and completely de-aerated by bubbling purified hydrogen through them for ten minutes before recording the polarograms. In order to establish whether the waves are diffusion-controlled the effects of mercury pressure ($h_{corr.}$) and rhenium(VII) concentration ($C$) on the wave height($i_d$) were critically examined.[5] For diffusion-controlled waves (i.e. those for which both $i_d/h^{\frac{1}{2}}_{corr.}$ and $i_d/C$ are constant under the usual conditions within limits of experimental error) the number of faradays consumed per mole of rhenium(VII) undergoing reduction was determined by applying the Ilkovic equation.[5] For the diffusion-controlled waves, reversibility of the electrode process was tested by evaluating the slope of the logarithmic plot (which is $0{\cdot}06/n$ at 25°C for a reversible electrode process consuming $n$ faradays per mole), the intercept of which gave the accurate value of the half-wave potential ($E_{\frac{1}{2}}$).[5]

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(1) J. HEYROVSKY, *Nature, Lond.* **135,** 870 (1935).
(2) J. J. LINGANE, *J. Amer. Chem. Soc.* **64,** 1005 (1942).
(3) J. J. LINGANE, *J. Amer. Chem. Soc.* **64,** 1001 (1942); C. L. RULFS, and P. J. ELVING, *J. Amer. Chem. Soc.* **73,** 3284 (1951).
(4) R. COLTON, J. DALZIEL, W. P. GRIFFITH and G. WILKINSON, *J. Chem. Soc.* (*Lond.*) 71 (1960).
(5) I. M. KOLTHOFF, and J. J. LIGANE, *Polarography*, Vol. 1. Interscience, New York (1952).

## RESULTS

*Sodium perchlorate, potassium iodide, potassium thiocyanate and potassium oxalate media.* In all these media reduction of rhenium(VII) begins at ca. −1·4 V vs. S.C.E. (Fig. 1). However in each case the limiting current is much higher than even that expected for a reduction of rhenium(VII) to rhenium (−I). None of the results showed any interesting features which might be of practical use, and further detailed investigations of these waves were not undertaken.

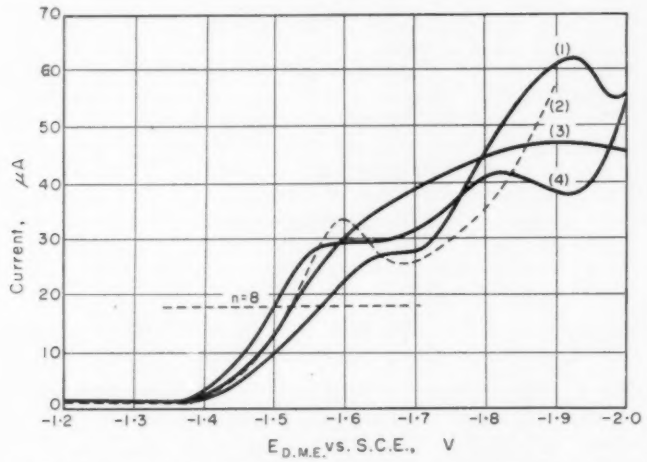


FIG. 1.—Polarograms of rhenium(VII) in different media. $KReO_4$, 0·5 mM; $m^{2/3}t^{1/6}$, 1·996 ± 0·005 $mg^{2/3}$ $sec^{-1/2}$ at −1·65 volt vs. S.C.E.; Temp., 25°C.
(1) $NaClO_4$, (2) KI, (3) KSCN, (4) $K_2C_2O_4$; each one 0·5 M.

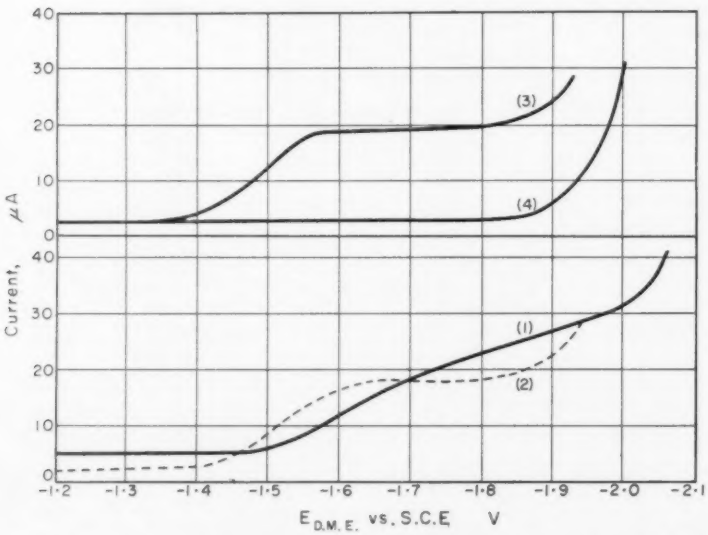


FIG. 2.—Polarograms of rhenium(VII) in cyanide media (curves 1–3). $KReO_4$, 0·5 mM; $m^{2/3}t^{1/6}$, 1·993 ± 0·005 $mg^{2/3}$ $sec^{-1/2}$ at −1·65 volt vs. S.C.E.; Temp., 25°C.
(1) 0·1 M KCN*, (2) 0·5 M KCN, (3) 1 M KCN, (4) Cyanide blank (1 M KCN). (* We have recorded this to confirm the findings of COLTON *et al.*: ref. 4 in text.)

*Potassium cyanide medium.* Recently COLTON *et al.*[4] reported a two-step reduction of perrhenate ion in 0·1 M potassium cyanide, which they assigned to the reduction of rhenium(VII) first to rhenium(V) and then to rhenium(−I). These waves are ill-defined, and potassium cyanide at that concentration is not a good supporting electrolyte for the polarographic reduction of rhenium(VII). It has been observed during the present investigations that at cyanide concentrations of 0·5 M and over, up to at least

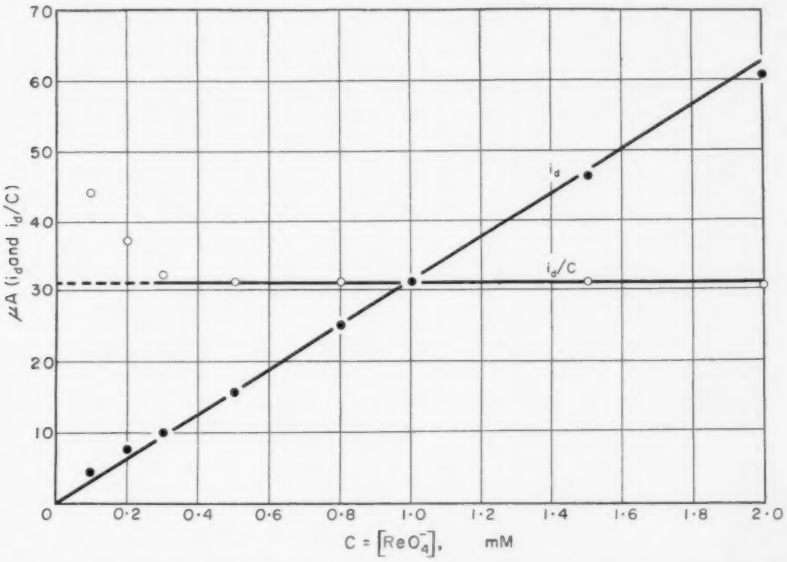


FIG. 3.—Dependence of diffusion current on rhenium(VII) concentration in cyanide medium (1 M KCN). $m^{2/3}t^{1/6}$, 1·993 ± 0·003 $mg^{2/3}$ $sec^{-1/2}$; Temp., 25°C.

2 M potassium cyanide, rhenium(VII) gives a single well-defined and diffusion-controlled wave originating at ca. −1·4 V vs. S.C.E., with $E_{\frac{1}{2}} \simeq -1{\cdot}5$ V on the same scale. Some of these polarograms are shown in Fig. 2. In the range of cyanide concentration mentioned above the height of the wave has been found to be independent of cyanide concentration and proportional to the square root of the effective pressure of mercury ($h^{\frac{1}{2}}_{\text{corr.}}$, i.e. $m^{2/3}t^{1/6}$). The limiting current ($i_d$) for this wave varies linearly with the concentration of rhenium(VII) and $i_d/C$ is constant (31·3 μA/mM under the experimental conditions) from 0·3 to at least 2·0 mM perrhenate ion (Fig. 3). The wave is irreversible but diffusion-controlled, and $n$ has an average value of 6·9 for different rhenium(VII) concentrations, indicating thereby a reduction of rhenium (VII) to rhenium(O) in this medium. Furthermore, $E_{\frac{1}{2}}$ has been found to shift from −1·5 V to −1·46 V, both vs. S.C.E., with a change in cyanide concentration from 0·5 to 2·0 M.

## DISCUSSION

Of the various media investigated only potassium cyanide at a concentration of $\geqslant$0·5 M appears to be suitable for the polarographic determination of rhenium after conversion to perrhenate ion. The shift of $E_{\frac{1}{2}}$ to a more negative potential with increasing cyanide concentration may possibly be due to stablization of rhenium(O) by

complexing with cyanide ion. This is not unlikely,[6] in view of the existence of a cyanide complex of manganese(I) and manganese(O).[7]

The unusually large values of the limiting currents in the reduction waves of rhenium(VII) in sodium perchlorate, potassium iodide, potassium thiocyanate and potassium oxalate media are possibly due to the catalytic nature of these waves. Similar catalytic waves have been observed by earlier workers in several other media.[1,2,3a]

*Acknowledgement*—The investigations reported above were carried out in the Inorganic Chemistry Department of the Indian Association for the Cultivation of Science, Calcutta, for which our thanks are due to the Director of the Institute.

[6] VON D. CLAUSS and A. LISSNER, *Z. Anorg. Chem.* **297**, 300 (1958).
[7] V. J. CHRISTENSEN, J. KLEINBERG and A. W. DAVIDSON *J. Amer. Chem. Soc.* **75**. 2495 (1953).

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# STUDIES IN HEAVY METAL SOAPS—I MOLECULAR WEIGHTS OF SOME COPPER *n*-ALKANOATES

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(*Received* 29 *January* 1961; *in revised form* 19 *March* 1961)

**Abstract**—Copper alkanoates have been found to show considerably low values of magnetic susceptibility compared to other copper salts. Two alternative explanations based on formation of chelate rings either on a monomeric or dimeric structure, have been suggested for the above observations. The crystal structure as well as partition coefficients experiments tend to support the latter view. Actual measurements of molecular weights ebullioscopically in benzene employing a sensitive thermistor for elevations of temperature have confirmed the dimeric nature of the following soaps—butyrate laurate, palmitate and stearate of copper in chloroform and benzene.

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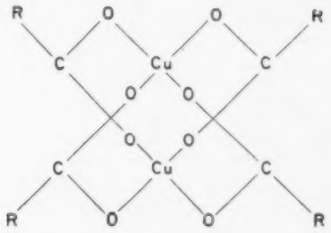
THE magnetic susceptibilities of copper *n*-alkanoates, measured systematically by AMIEL,[1] indicated much lower values compared to those normally observed for other copper (II) salts. The following bimolecular structure in the solid state has been




claimed by NICKARK and SKOENING.[2] MARTIN and WATERMANN[3] have tried to explain the low values of magnetic susceptibility on the basis of above dimeric structure. The dimeric structure has also been indirectly assumed to explain the partition coefficient values of copper propionate between water and chloroform.[4] NELSON and PINK[5] have investigated the micellar and molecular weights of some metal soaps in toluene, isobutyl alcohol and pyridine, and found that molecules exhibit a high degree of aggregration in organic solvents. In a detailed study of copper (II) alkanoates, MARTIN and WHITLEY[6] have shown that cyroscopic measurements in dioxan confirmed the dimeric structure. However, amongst the non-ionising solvents tried[6] for ebullioscopic measurements dioxan appeared to decompose the copper alkanoates, whereas the elevations of the boiling point of benzene were remarkably small indicating molecular complexities of about six to eight.

In view of a detailed scheme to investigate the behaviour of heavy metal soaps in solutions, it was considered of interest to remeasure the molecular weights of copper alkanoates ebullioscopically in some suitable solvents. The solubility of copper alkanoates was sufficiently high in dioxane and pyridine but these solvents were not

[1] AMEIL, *C. R. Acad. Sci., Paris* **207**, 1097 (1938).
[2] NICKARK and SKOENING, *Acta Cryst.* **6**, 227 (1953).
[3] MARTIN and WATERMANN, *J. Chem. Soc.* 2547 (1957).
[4] D. P. GRADDON, *J. Inorg. Nucl. Chem.* **11**, 337 (1959).
[5] NELSON and PINK, *J. Chem. Soc.* 1744 (1952).
[6] MARTIN and WHITLEY, *J. Chem. Soc.* 1394 (1958).

employed due to the possibility of formation of addition compounds with the dissolved alkanoates. Among the other solvents attempted, the solubility in acetone was too low for accurate measurements of elevations of boiling points but benzene and chloroform were found to be suitable. Critical solution phenomenon was observed in both the solvents. Values of critical solution temperature (C.S.T.) for copper stearate were estimated to be approximately 45°C and 65°C in chloroform and benzene respectively. The molecular complexity of the soaps appeared to be highly susceptible to even traces of moisture but provided careful precautions were taken to exclude moisture, the ebullioscopic molecular weights of copper alkanoates (butyrate to strearate) corresponded to dimeric structure in both the solvents (Table 1).

TABLE 1.

| Name | Molecular formula | Formula weight | Molecular weight in benzene | Molecular weight in chloroform |
|---|---|---|---|---|
| Copper butyrate | $Cu(C_3H_7COO)_2$ | 237·54 | 514·6 | 520·0 |
| Copper laurate | $Cu(C_{11}H_{23}COO)_2$ | 461·54 | 857·8 | 980·0 |
| Copper palmitate | $Cu(C_{15}H_{31}COO)_2$ | 573·54 | 1286·0 | 1108·0 |
| Copper stearate | $Cu(C_{17}H_{35}COO)_2$ | 629·54 | 1103·0 | 1162·0 |

## EXPERIMENTAL

Copper laurate, stearate and palmitate were prepared by metathesis of alcoholic copper acetate (Analar, B.D.H.) with an alcoholic solution of redistilled acids (Palmitic acid, B.D.H. b.p., 222 ± 0·5°C/16 mm, stearic acid, B.D.H., b.p., 228 ± 0·5°C/10 mm). The precipitates were washed with conductivity water and then with alcohol to remove excess of free acids and other impurities, and were dried over sulphuric acid under vacuum for two to three days. The compounds were recrystallised from dry dioxane and excess of solvent was removed at 70–75°C under 2 mm pressure. Copper butyrate was prepared by treating copper carbonate with an excess of dilute butyric acid and was purified by repeated crystallization.[7]

The measured molecular weights were found to be highly susceptible to moisture. Extra precautions had, therefore, to be taken to make the solvents (benzene and chloroform) anhydrous and to exclude moisture during the time of measurements.

The molecular weights of the compounds were determined by a semi-micro ebulliometer (Gallenkamp), employing thermistor sensing. The apparatus requires 4–5 hr for each determination, therefore precautions were taken to protect the solvent and the sample from moisture. Standard joints were, therefore, used in the ebulliometer bulb which was attached to a standard joint condenser, which in turn was protected from moisture by anhydrous calcium chloride. The resistance bridge was attached with a separate sensitive Pye Scalamp Galvanometer (Cat. No. 1904/5).

The metal contents of the compounds were determined and the results are shown below:

TABLE 2.

| Name | Molecular formula | Cu found (%) | Cu calc. (%) |
|---|---|---|---|
| Copper butyrate | $Cu(C_3H_7COO)_2$ | 26·67 | 26·70 |
| Copper laurate | $Cu(C_{11}H_{23}COO)_2$ | 13·72 | 13·77 |
| Copper palmitate | $Cu(C_{15}H_{31}COO)_2$ | 11·11 | 11·08 |
| Copper stearate | $Cu(C_{17}H_{35}COO)_2$ | 10·17 | 10·09 |

[7] R.L. MARTIN and H. WATERMANN, *J. Chem. Soc.* 2545 (1957).

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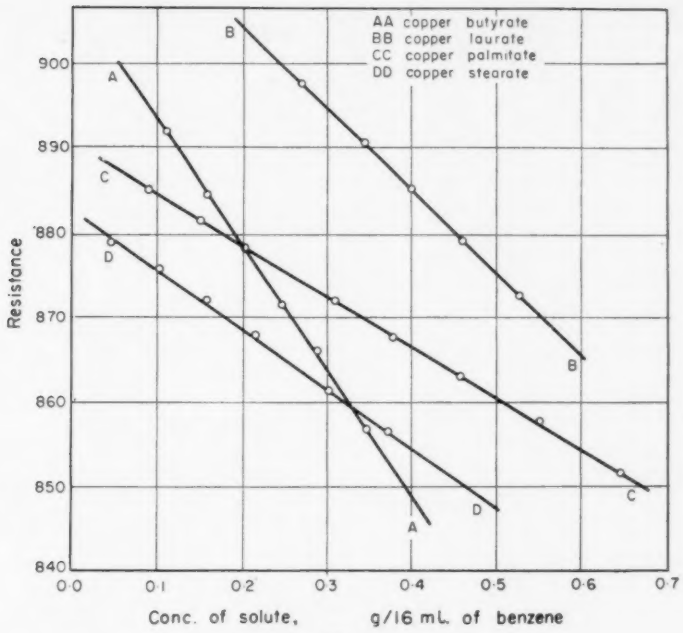


FIG. 1.

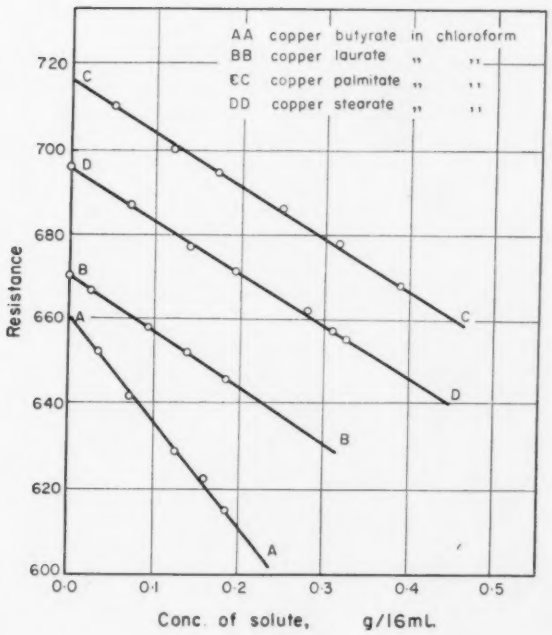


FIG. 2.

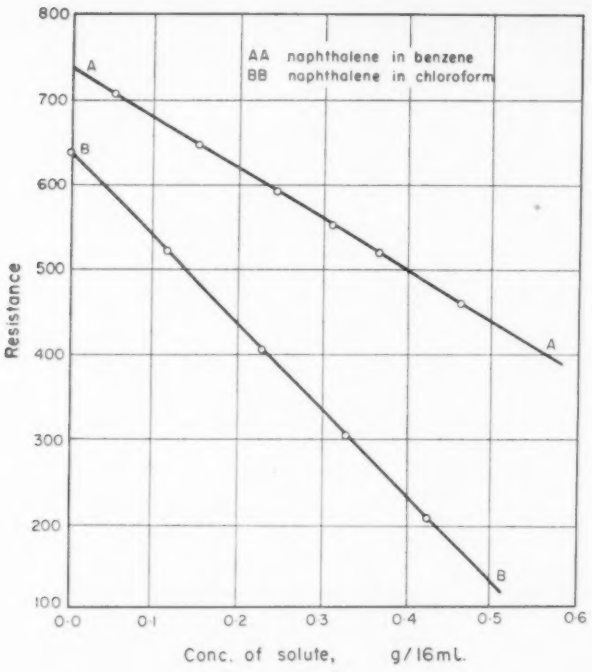


FIG. 3.

For molecular weight determination, 16 ml of dry benzene or chloroform was used each time. It was observed that stable observations can only be obtained after addition of some solute with benzene as a solvent, whereas no such addition was required with chloroform. The change in values of the resistance of the solution with concentration is shown in Figs. 1 and 2. The molecular weight can be calculated by the simple relationship, $M = KW/R$ where $M$ is molecular weight of the dissolved substance, $W$ is the weight of the solute, $R$ is the decrease in resistance due to addition of $W$ of solute and $K$ is a constant for the solvent. In view of the linear relationship between $W$ and $R$ (Figs. 1 and 2), the graphical method for the calculation of molecular weights has been employed, according to which $M = Km$, where $m$ is the slope of the line. All the resistances were measured within an accuracy of $\pm 0{\cdot}20\ \Omega$. The values for $K$ were taken to be 77,200 for benzene and 127,400 for chloroform after several determinations with naphthalene as solute (Fig. 3).

*Acknowledgement*—The authors are grateful to the Council of Scientific and Industrial Research, New Delhi, for a research fellowship to one of them (A. K. R.) during the tenure of which the present investigations were carried out.

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# ION-EXCHANGE ADSORPTION OF ZINC AND COPPER IONS ON SILICA

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**Abstract**—Ion-exchange adsorption of zinc and copper ions on silica were examined in 2 M $NH_4Cl$ solution containing ZnO or $ZnCl_2$ and in 1 M $NH_4Ac$ containing 0·05 M $CuCl_2$ respectively. The ion-exchange adsorption attains equilibrium in about 2 hr at 25°C. The adsorption of zinc ion increases with the pH of the solution up to pH 7·12, then decreases. Between pH 5·48 and 6·38 the mole-ratio of $H^+$ released/$Zn^{2+}$ adsorbed is constant at about 3·0. Zinc ion adsorption on heated silica decreases markedly with increase in the heating temperature. For copper ion adsorption, the mole-ratio, $H^+$ rel./$Cu^{2+}$ ads., is 4·0. The infra-red absorption spectra of silica samples, heated silica and silica treated with $Zn^{2+}$, $Cu^{2+}$ and $Na^+$ solutions, were taken. A decrease in the absorption intensities for the bending vibration of −OH groups on the silica is discussed. A surface complex mechanism for metal ion adsorption of silica is proposed and it is concluded that the silica surface is acting as tridentate ligands for the zinc ion adsorption. A new method for determination of the surface acid and the surface area of silica is suggested.

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PREVIOUSLY the author examined an ion-exchange property of manganese dioxide,[1] and proposed a surface complex formation for the zinc ion adsorption. The surface of the manganese dioxide was considered to act as a bidentate ligand forming a six membered ring with an adsorbed zinc ion.

In the present investigation silica was chosen in order to examine further the applicability of the surface complex mechanism.

The surface acidity of silica and silica–alumina is well known and has been frequently studied.[2,3,4,5] As metal ions to be adsorbed on silica, zinc and copper ions were chosen because both form tetraco-ordinated complexes of bivalent ions, but differ in the steric structure. Zinc ion forms tetrahedral complexes and copper ion square planar complexes.

## EXPERIMENTAL AND DISCUSSION

### *Samples*

Two silica samples were used, reagent silica powder and powdered silica gel (made by Mallinckrodt Chemical Works, U.S.A.) for chromatographic use, denoted $SiO_2(R)$ and $SiO_2(C)$ respectively.

### *Surface acid of silica*

The surface of silica reacts with $OH^-$ at pH values below those required for dissolution. This is the so-called "surface acidity" of silica. The surface acidity of

[1] A. KOZAWA, *J. Electrochem. Soc.* **106**, 552 (1959).
[2] G. W. SEARS, *Analyt. Chem.* **28**, 1981 (1956).
[3] V. HOLM, G. BAILEY and A. CLARK, *J. Phys. Chem.* **63**, 129 (1959).
[4] J. E. MAPES and R. P. EISCHENS, *J. Phys. Chem.* **58**, 1059 (1954).
[5] M. OKUDA and T. TACHIBANA, *Bull. Chem. Soc., Japan* **33**, 863 (1960).

silica,[2] and also of other inorganic solids such as tungsten (VI) and molybdenum (VI) oxides[6,7] has been investigated by neutralizing with sodium hydroxide solution.

In the previous study of manganese dioxide,[1] when the sample was shaken with a zinc solution, (2M $NH_4Cl$ containing dissolved ZnO), zinc ion was adsorbed and considerable hydrogen ion was released. The mole-ratio of the $H^+$ released to the $Zn^{2+}$ adsorbed was 2:1. An important advantage of using the zinc solution is in that a nearly constant pH can be maintained even though considerable $H^+$ ion is released and still the released $H^+$ can be determined by a simple titration.

The surface acid of the silica samples was determined by two methods.

TABLE 1.—SURFACE ACID OF A 2·00 g SAMPLE OF SILICA

| Sample | NaOH method | $Zn^{2+}$ solution method | | |
|---|---|---|---|---|
| | $H^+$ neutralized (mole) | $H^+$ released (mole) | $Zn^{2+}$ adsorbed (mole) | $H^+$ rel./$Zn^{2+}$ ads. |
| $SiO_2(R)$ | $1{\cdot}57 \times 10^{-3}$ | $3{\cdot}57 \times 10^{-3}$ | $1{\cdot}23 \times 10^{-3}$ | 2·99 |
| $SiO_2(C)$ | 2·19 | 9·00 | 3·00 | 3·00 |

(1) NaOH method: A 2·00 g sample was mixed with 25 ml of 0·1 N NaOH solution in an Erlenmyer flask with a rubber stopper. It was occasionally shaken manually for 12 hr at room temperature, which was not far from 25°C. Then 5 ml of the supernatant solution was titrated with 0·100 N HCl.

(2) The $Zn^{2+}$ solution method: A 2·00 g sample was mixed with 25 ml of the $Zn^{2+}$ solution (2·0 M $NH_4Cl$, 0·1 M ZnO, pH 6·8) in a 100 ml flask with a rubber stopper. It was shaken for more than 6 hr and allowed to stand overnight. Then 5 ml portions of the supernatant solution were analysed for $Zn^{2+}$ by titrating with 0·05 M EDTA standard solution using Eriochrom black T as the indicator ($NH_4Cl$—$NH_4OH$ buffer was used to adjust pH to 9–10) and for $H^+$ by titrating with 0·100 N HCl solution using methyl orange as the indicator, respectively. Also, 5 ml portions of the original $Zn^{2+}$ solution were titrated in the same manner. From the differences between the amounts of EDTA and HCl solutions required by the test solution and the original $Zn^{2+}$ solution, the amounts of $Zn^{2+}$ ion adsorbed and $H^+$ ion released were determined.

The results are shown in Table 1. The surface acid determined by the $Zn^{2+}$ solution method was much more than that by the NaOH method, though the NaOH solution was much higher in pH value than the $Zn^{2+}$ solution. Another significant fact is that the mole-ratio of $H^+$ rel./$Zn^{2+}$ ads. is 3·0 for both samples. This means that all the surface acid of silica cannot be neutralized by an alkaline solution, but zinc ion can exchange with the hydrogen ion, forming a surface complex as shown in equation (2) in Table 8 which will be discussed below. This also suggests that in order to determine the total acid or exchangable hydrogen of a silica surface a neutralization method by an alkaline solution has little value, and a better method based on surface complexing is needed. The author would like to recommend the $Zn^{2+}$ solution method for the time being.

*Ion-exchange adsorption rate of $Zn^{2+}$ ion on silica*

Samples of 1·00 g of $SiO_2(C)$ were treated with 25 ml of a zinc solution (2 M $NH_4Cl$, 0·1 M $ZnCl_2$, $NH_3$, pH 6·8). The mixtures were shaken manually every 5 min at 25 and 45 ± 0·5°C. At the times indicated in Table 2, a mixture was centrifuged and the supernatant solution was analysed for zinc. The zinc adsorption is shown in Table 2, from which it is clear that the ion-exchange adsorption of zinc ion reaches equilibrium in 120 minutes at 25°C and in 45 min at 45°C.

[6] M. L. FREEDMAN, *J. Amer. Chem. Soc.* **81**, 3834 (1959).
[7] M. L. FREEDMAN, *Analylt. Chem.* **32**, 637 (1960).

*Effect of pH.* Seven $Zn^{2+}$ solutions with varying pH were made by adding 6–50 ml of 28% $NH_3$ solution to 1l. of 2 M $NH_4Cl$ containing 0·1 M $ZnCl_2$. Samples of 1·00 g of $SiO_2(C)$ or 2·00 g of $SiO_2(R)$ were shaken with 25 ml portions of these seven solutions in 100 ml Erlenmeyer flasks for several hours at room temperature. Then the mixtures were centrifuged, and 5 ml portions of the solutions were analysed to determine the $Zn^{2+}$ ion adsorption and the $H^+$ ion liberation.

TABLE 2.—$Zn^{2+}$ ADSORPTION RATE ON $SiO_2(C)$

| Temp. (°C) | Time (min) | $Zn^{2+}$ adsorbed (mole/g) |
|---|---|---|
| 25°C | 5 | $1{\cdot}30 \times 10^{-3}$ |
| 25 | 15 | 1·33 |
| 25 | 60 | 1·38 |
| 25 | 120 | 1·40 |
| 25 | 210 | 1·40 |
| 45 | 20 | 1·38 |
| 45 | 45 | 1·40 |

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TABLE 3.—ION-EXCHANGE ADSORPTION OF $Zn^{2+}$ ON $SiO_2$ AT VARIOUS pH VALUES

| Sample | pH (initial) | pH (final) | $Zn^{2+}$ conc.* (mole/l.) | $H^+$ released (mole) | $Zn^{2+}$ adsorbed (mole) | $H^+$ rel./$Zn^{2+}$ ads. |
|---|---|---|---|---|---|---|
| 2·00 g of $SiO_2(R)$ | 6·15 | 5·65 | 0·0782 | $0{\cdot}845 \times 10^{-3}$ | $0{\cdot}305 \times 10^{-3}$ | 2·78 |
| | 6·29 | 5·80 | 0·0740 | 1·56 | 0·525 | 2·97 |
| | 6·60 | 6·15 | 0·0554 | 2·49 | 0·885 | 2·82 |
| | 6·80 | 6·48 | 0·0430 | 3·57 | 1·14 | 3·17 |
| | 7·40 | 7·20 | 0·0328 | 5·15 | 1·41 | 3·68 |
| | 7·74 | 7·63 | 0·0355 | 5·31 | 1·27 | 4·02 |
| | 8·30 | 8·20 | 0·0395 | 6·05 | 1·18 | 5·13 |
| 1·00 g of $SiO_2(C)$ | 6·15 | 5·48 | 0·0770 | 0·985 | 0·335 | 2·94 |
| | 6·29 | 5·65 | 0·710 | 1·83 | 0·600 | 3·06 |
| | 6·60 | 5·90 | 0·0515 | 2·84 | 0·983 | 2·90 |
| | 6·80 | 6·38 | 0·0318 | 4·29 | 1·42 | 3·01 |
| | 7·40 | 7·12 | 0·0134 | 6·65 | 1·90 | 3·50 |
| | 7·77 | 7·67 | 0·0180 | 6·72 | 1·71 | 3·97 |
| | 8·30 | 8·20 | 0·0238 | 7·48 | 1·58 | 4·73 |

* $Zn^{2+}$ concentration of the bulk solution at equilibrium.

The results are shown in Table 3 in which pH and zinc ion concentration of the bulk solution at equilibrium are also shown. According to Table 3, when the zinc solution has an equilibrium pH below 6·4, the ratio of $H^+$ released to $Zn^{2+}$ adsorbed is very close to 3·0 for both silica samples, though the ion-exchange adsorption of zinc ion increases markedly with the pH of the solution.

In the above experiments, two reactions for $H^+$ ion liberation are possible, ion exchange by zinc ion and that by ammonium ion. In order to examine $H^+$ ion liberation by ammonium ion, 1·00 g of $SiO_2(C)$ was shaken thoroughly with 25 ml of 2 M $NH_4Cl$ solution having various pH values which were adjusted by adding ammonia. Then 5 ml portions of the solutions, obtained by centrifuging, were titrated with 0·100 N HCl solution. From a difference between the amount of the HCl consumed by this titration and the amount consumed by a titration of 5 ml of the original solution, $H^+$ ion liberation was determined. The results are shown by the dashed line in Fig. 1, in which $Zn^{2+}$ adsorption and $H^+$ liberation of 1·00 g of $SiO_2(C)$ (data in

Table 3) is also shown for comparison. It is clear in Fig. 1 that $H^+$ released by $NH_4^+$ ion adsorption in the $NH_4Cl$ solution is only 10–15 per cent of the $H^+$ released in the zinc solution. When the solution contains zinc ion most of the adsorption sites on the silica surface will be occupied by zinc and the contribution to the $H^+$ ion liberation by $NH_4^+$ adsorption is probably negligibly small.

It is also seen in Fig. 1 that at pH higher than 7·5 $Zn^{2+}$ adsorbed begins to decrease and $H^+$ released to increase, probably due to high stability of the $[Zn(NH_3)_4]^{2+}$

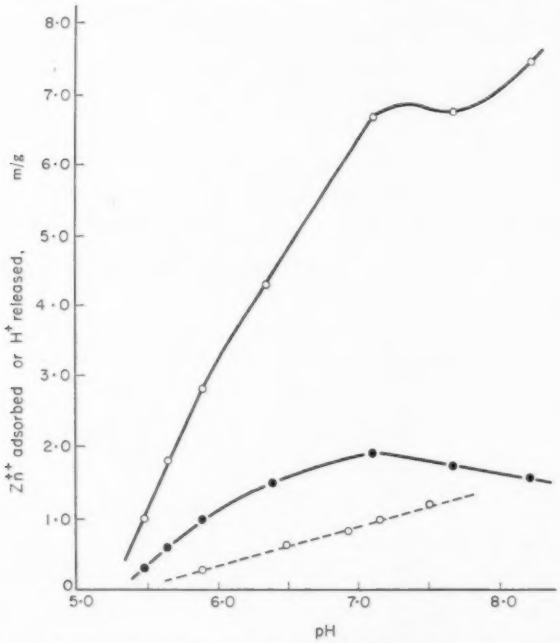


FIG. 1.—Ion-exchange adsorption of $Zn^{2+}$ on $SiO_2(C)$ in the $Zn^{2+}$ solution (2 M $NH_4Cl$, 0·1 M $ZnCl_2$, varying amounts of ammonia added) and $H^+$ liberation by $NH_4^+$ adsorption in $NH_4Cl$ solution with various pH values. ○: $H^+$ released in the $Zn^{2+}$ solution, ●: $Zn^{2+}$ adsorbed, the dashed line : $H^+$ released in the $NH_4Cl$ solution. Abscissa shows pH of the bulk solution at equilibrium.

complex at higher pH values and increase of an ion-exchange reaction by $NH_4^+$ ion.

At the maximum shown on the curve of $Zn^{2+}$ adsorbed in Fig. 1, $6{\cdot}65 \times 10^{-3}$ mole of $H^+$ ion was liberated from one gramme of the sample which had 1110 $m^2$ in surface area, as shown below. A silica surface has about eight Si—OH groups[8] per $(m\mu)^2$. Therefore under this condition (pH 7·10), about half of the total Si—OH groups co-ordinate with $Zn^{2+}$ releasing the $H^+$ ion, since the total Si-OH for 1110 $m^2$ amounts to $88 \times 10^{20}/6 \times 10^{23} = 15 \times 10^{-3}$ mole.

### *Ion-exchange adsorption of zinc ion on heated* $SiO_2(C)$

Samples of $SiO_2(C)$ were heated at 400, 600 and 800°C for 3 hr in an electric furnace. The heated samples were kept in glass bottles with good stoppers to prevent adsorption of moisture. The ion-exchange adsorption of these heated samples was measured in the manner described above, using two zinc solutions as shown in Table 4.

[8] R. K. ILER, *The Colloid Chemistry of silica and silicates* p. 100. Cornell University Press, Ithaca, N.Y. (1955).

The results are shown in Table 4 in which the water contents of these samples are also shown. It is clear that the mole-ratio, $H^+/Zn^{2+}$, keeps a constant value close to 3·0, though the absolute values of the $Zn^{2+}$ adsorbed and the $H^+$ released decrease markedly with the increase of heating temperature and the decrease of water content. For comparison $Zn^{2+}$ adsorption and $H^+$ liberation at pH 6·0 were obtained from the data in Table 4 by graphical interpolation, and then they were corrected for water

TABLE 4.—ION-EXCHANGE ADSORPTION OF ZINC ION ON HEATED $SiO_2(C)$

| Sample | Water* content (%) | Solution‡ | $Zn^{2+}$ conc.† (mole/l.) | pH† | $H^+$ released (mole/g) | $Zn^{2+}$ adsorbed (mole/g) | $H^+/Zn^{2+}$ |
|---|---|---|---|---|---|---|---|
| 1 $SiO_2(C)$ not heated | 13·1 | a | 0·0698 | 5·60 | $1·79 \times 10^{-3}$ | $0·593 \times 10^{-3}$ | 3·02 |
| 2 $SiO_2(C)$ not heated | | b | 0·0432 | 6·01 | 3·68 | 1·24 | 2·97 |
| 3 $SiO_2(C)$ heated at 400°C | 5·80 | a | 0·0710 | 5·60 | 1·73 | 0·563 | 3·07 |
| 4 $SiO_2(C)$ heated at 400°C | | b | 0·0455 | 6·10 | 3·52 | 1·18 | 2·98 |
| 5 $SiO_2(C)$ heated at 600°C | 1·40 | a | 0·0735 | 5·70 | 1·57 | 0·500 | 3·14 |
| 6 $SiO_2(C)$ heated at 600°C | | b | 0·0540 | 6·45 | 2·97 | 0·970 | 3·06 |
| 7 $SiO_2(C)$ heated at 800°C | 0·40 | a | 0·0802 | 6·00 | 1·05 | 0·333 | 3·15 |
| 8 $SiO_2(C)$ heated at 800°C | | b | 0·0698 | 6·60 | 1·70 | 0·575 | 2·96 |

* Determined from weight loss when the sample was ignited in a crucible for more than 3 hr.
† Zinc ion concentration and pH of the bulk solution at the ion-exchange equilibrium.
‡ Solution (a): 2 M $NH_4Cl$, 0·0935 M $ZnCl_2$, ammonia added, pH 6·25.
Solution (b): 2 M $NH_4Cl$, 0·0928 M $ZnCl_2$, ammonia added, pH 6·63.

content in order to obtain values for 1·00 g of net silica. The final results are shown in Fig. 2.

The dashed line in Fig. 2 indicates the maximum $H^+$ liberation when it is assumed that the exchangeable hydrogen on the silica surface comes from some kind of combined water corresponding to the water content shown in Table 4. At 600- and 800-heated points, more $H^+$ than the hydrogen of the combined water was liberated as can be seen in Fig. 2. This may mean that in the first step of the ion exchange reaction for the heated sample hydration of the silica occur to make Si—OH groups on the surface. Of course silica is a sort of polyacid resulting from condensation of silicate ions, therefore most of the surface of silica not heated excessively should be covered with the Si—OH groups. It is said that the dehydration of the —OH groups on the silica surface starts at 300–400°C[9]

An explanation of the marked decrease in the ion-exchange adsorption by heating shown in Fig. 2 cannot be given at the present time. Decrease of the surface area due to heating and/or irreversibility of the rehydration of the surface are possibilities.

*Possibility of surface area measurement by the $Zn^{2+}$ adsorption*

SEARS[2] proposed a method to determine the surface area of various silica samples, and showed experimentally that the surface areas of silica samples (including heated silica up to 450°C) measured by the BET method can be correlated with the titration value, $V$, by the following equation:

$$S = 32V - 25$$

where $S$ is surface area ($m^2/g$) and $V$ is the titration value for a 1·50 g sample of silica.

[9] R. S. MCDONALD, *J. Phys. Chem.* **62**, 1168 (1958); B. A. NIKITIN, A. N. SIDOROB and A. B. KARYAKIN, *Zh. Fiz. Khim.* **30**, 117 (1956); M. M. EGOROB, K. R. KRASILNIKOB, and E. A. SYSOEB, *Dokl. Akad. Nauk. S.S.S.R.* **108**, 103 (1956).

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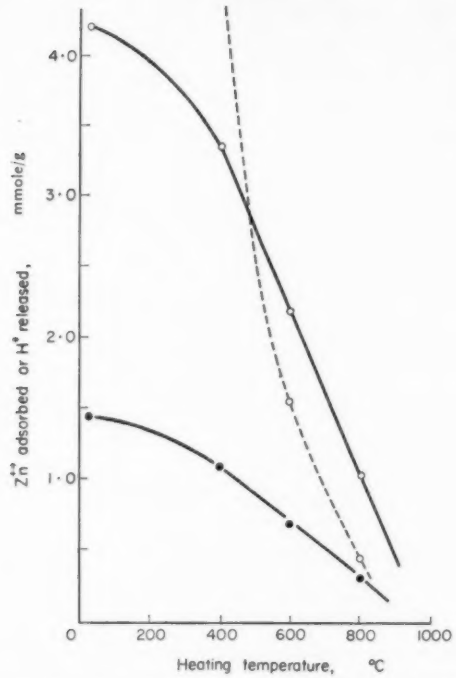


FIG. 2.—Ion-exchange adsorption of $Zn^{2+}$ on $SiO_2(C)$ heated up to 800°C. The data at pH 6·0 were obtained from those shown in Table 4 by interpolation. ○: $H^+$ released, ●: $Zn^{2+}$ adsorbed. The dashed line shows possible maximum $H^+$ calculated from the water content values shown in Table 4.

$V$ was obtained as follows. A sample containing 1·50 g of silica is acidified with dilute hydrochloric acid to a pH of 3–3·5. To this solution is added 30 g of sodium chloride and the volume is made up to 150 ml with distilled water. The solution is titrated with 0·10 N NaOH at 25°C. The pH is measured with a glass electrode through the titration. The titer $V$ is the volume of 0·1 N NaOH in ml required to raise the pH from 4·0 to 9·0.

The surface areas of the two samples, $SiO_2(R)$ and $SiO_2(C)$, were determined by the SEARS' method. The results and the ratio of the surface area to the $Zn^{2+}$ adsorption (values in Table 1) are shown in Table 5. The ratio, $S_{SEARS}/Zn^{2+}$ ads., for the two kind

TABLE 5.—SURFACE AREA OF SILICA

| | $S_{SEARS}$ ($m^2/g$) | $Zn^{2+}$ adsorbed (mole/2·0 g) | $S_{SEARS}/Zn^{2+}$ ads. |
|---|---|---|---|
| $SiO_2(R)$ | 445 | $1·23 \times 10^{-3}$ | $7·24 \times 10^5$ |
| $SiO_2(C)$ | 1110 | 3·00 | 7·40 |

* Surface area by SEARS method, which corresponds to the surface area by the BET method.

of silica samples agree with each other. This suggests a possibility of using the $Zn^{2+}$ solution method for the surface area determination. The $Zn^{2+}$ adsorption for a given

sample measured as described may be correlated to the surface area of the sample from the BET method by a following equation,

$$S(m^2) = 7{\cdot}3 \times 10^5 \times (Zn^{2+} \text{ ads. in mole})$$

This method might not apply to silica samples heated over 450°C.

### $Cu^{2+}$ *ion adsorption on silica*

A weighed sample of $SiO_2(C)$ was shaken with 50 ml of a $Cu^{2+}$ solution (1 M $NH_4Ac$, 0·05 M $CuCl_2$, $NH_3$, pH 6·50) in a stoppered Erlenmeyer flask for about 6 hours at room temperature. Then the mixture was centrifuged and a 10 ml portion of the solution was titrated with 0·100 N HCl solution the pH being measured by a glass electrode pH meter until the pH was 2·0. Also, 10 ml of the original $Cu^{2+}$ solution was titrated in the same manner. From the difference of the two titration curves, $H^+$ liberation due to an ion-exchange of $Cu^{2+}$ ion was determined. In order to determine $Cu^{2+}$ ion another 10 ml portion of the centrifuged solution was titrated with 0·05 M EDTA using Pyrocatechol violet as the indicator.[10]

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The results are shown in Table 6, the most interesting fact is that the mol-ratio, $H^+$ rel./$Cu^{2+}$ ads., is very close to 4·0 though the absolute value of $Cu^{2+}$ adsorption varies from $0{\cdot}282 \times 10^{-3}$ mole to $0{\cdot}650 \times 10^{-3}$ mole for one gramme of $SiO_2(C)$.

### *Infra-red absorption of silica*

The infra-red absorption of $SiO_2(C)$ was measured by two methods.

(1) Nujol method: A 10 mg sample was thoroughly ground with 0·20 ml of Nujol in an agate mortar. The mixture was sandwiched between two sodium chloride plates, then the absorption curve was taken. Taking the absorption band of Nujol at 730 $cm^{-1}$ as an index of the thickness of the sample between the sodium chloride plates, the relative optical densities at 1075 $cm^{-1}$ and 963 $cm^{-1}$ for various silica samples were calculated by the base line method.[11] The results are shown in Table 7.

TABLE 6.—ION-EXCHANGE ADSORPTION OF $Cu^{2+}$ ON $SiO_2(C)$

| Sample taken (g) | pH* | $Cu^{2+}$ conc.* (mole/l.) | $Cu^{2+}$ adsorbed† (mole) | $H^+$ released (mole) | $H^+/Cu^{2+}$ |
|---|---|---|---|---|---|
| 0·500 | 6·40 | 0·0390 | $0{\cdot}325(0{\cdot}650) \times 10^{-3}$ | $1{\cdot}30 \times 10^{-3}$ | 4·00 |
| 1·00 | 6·38 | 0·0354 | 0·530(0·530) | 2·10 | 3·96 |
| 2·00 | 6·30 | 0·0311 | 0·743(0·372) | 3·00 | 4·04 |
| 3·00 | 6·18 | 0·0291 | 0·845(0·282) | 3·50 | 4·14 |

* pH and $Cu^{2+}$ concentration of the solution at the ion-change equilibrium.
† Values in parenthesis show $Cu^{2+}$ absorbed per 1·00 g of $SiO_2$ (*C*).

TABLE 7.—RELATIVE OPTICAL DENSITY FOR —OH BENDING VIBRATION OF VARIOUS SILICA SAMPLES (NUJOL METHOD)

| Absorption band ($cm^{-1}$) | $SiO_2(C)$ | $SiO_2(C)$ heated at 600°C | $SiO_2$—Zn* | $SiO_2$—Cu* | $SiO_2$—Na* |
|---|---|---|---|---|---|
| 730 | 0·20 | 0·20 | 0·20 | 0·20 | 0·20 |
| 963 | 0·26 | 0·20 | 0·214 | 0·198 | 0·230 |
| 1075 | 0·55 | 0·414 | 0·426 | 0·306 | 0·455 |

* These samples were prepared from $SiO_2(C)$ by shaking with the $Zn^{2+}$ solution (2M $NH_4Cl$, 0·1M ZnO pH 6·8), the $Cu^{2+}$ solution (1M $NH_4Ac$, 0·05M $CuCl_2$, ammonia added, pH 6·5) and 0·1N NaOH, respectively, then filtering and drying at 80°C.

[10] V. SUK and M. MALAT, *Chem. Anal.* **45**, 30 (1956).
[11] J. J. HEIGL, M. F. BELL and J. U. WHITE, *Analyt. Chem.* **19**, 293 (1947).

(2) KBr tablet method: A 0·333 mg silica sample was mixed with 200 mg of KBr powder and pressed to a tablet. The absorption curve was taken against a KBr tablet which had no silica sample. The results are shown in Fig. 3.

It was shown previously by infra-red absorption measurement of silica that most of the water in silica ($H_2O$ content: 12 per cent) exists as —OH groups.[12] Many inorganic compounds containing —OH groups such as α—AlOOH, α—FeOOH, $Zn(OH)_2$, $In(OH)_3$ etc., have infra-red absorption bands corresponding to the stretching

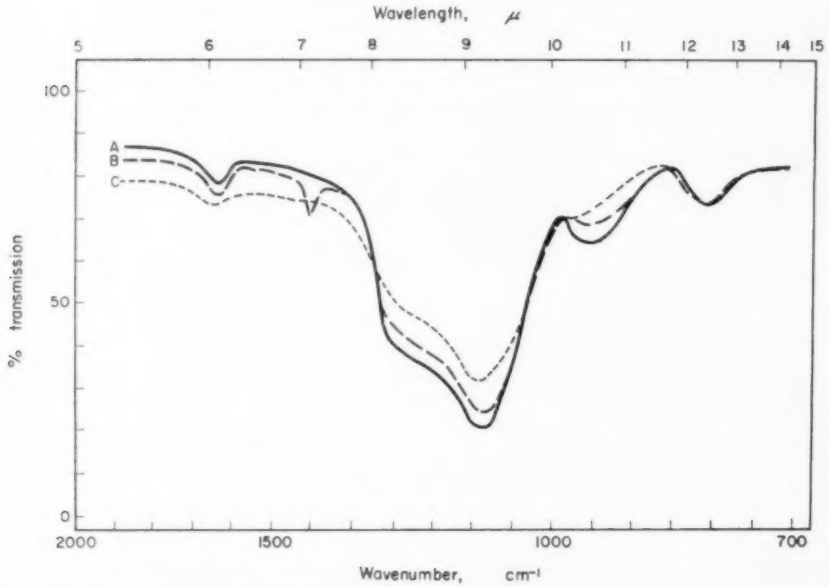


FIG. 3.—Infra-red adsorption of $SiO_2(C)$ by the KBr tablet method. A:$SiO_2(C)$, B:$SiO_2(C)$ treated with the $Zn^{2+}$ solution, C:$SiO_2(C)$ heated at 600°C.

and bending vibrations of —OH of around 3200 $cm^{-1}$ and 900–1100 $cm^{-1}$ respectively.[13] The latter usually show two or more absorption peaks. The absorption band due to the bending vibration of —OH group of iron (III) hydroxide was considered to be 1039 cm[14] and that of $Al_2O_3$ containing water to be 9·4–9·8μ (1065–1020 $cm^{-1}$).[12]

Taking these previous data into account, the absorption bands, 1090 $cm^{-1}$ and 950 $cm^{-1}$ shown in Fig. 3, or 1075 $cm^{-1}$ and 963 $cm^{-1}$ in the Nujol method may be considered to be bending vibrations of the —OH group on the silica surface. When the silica sample was heated at 600°C or treated with the zinc solution, the intensities of these bands decrease clearly compared to that of the original silica sample as shown in Fig. 3. As shown in Table 7, relative optical densities at 1075 $cm^{-1}$ and 963 $cm^{-1}$ obtained by the Nujol method also decrease when the sample was heated or treated with $Zn^{2+}$, $Cu^{2+}$, or NaOH solutions. These results of infra-red absorption are good evidence of the decrease of OH groups on a silica surface due to dehydration by

[12] O. GLEMSER and G. RIECK, *Z. Anorg. Chem.* **297**, 175 (1958).
[13] E. HARTERT and O. GLEMSER, *Z. Elektrochem.* **60**, 746 (1956).
[14] O. GLEMSER, D. K. KROON and C. V. D. STOLPE, *Nature, Lond.* **183**, 943 (1959).

heating or liberation of $H^+$ by ion-exchange adsorption of metal ions such as $Cu^{2+}$, $Zn^{2+}$ and $Na^+$.

## DISCUSSION

When divalent metal ions such as $Cu^{2+}$ and $Zn^{2+}$ which form tetra-co-ordinated complexes react with —OH groups on the silica surface forming a chelate structure, six cases are possible as shown in Table 8. Though OH, $H_2O$, Cl and $NH_3$ are possible ligands for a zinc ion in an aqueous $NH_4Cl$ solution, only Cl and $NH_3$

TABLE 8.—SURFACE COMPLEXES ON THE SILICA SURFACE

| | | | |
|---|---|---|---|
| (1) | —OH<br>—OH<br>—OH<br>—OH | + $MeCl_2$<br>+ $2NH_4Cl$ | —O<br>—O<br>—O—Me . . . $2NH_4^+$ + 4HCl<br>—O |
| (2) | —OH<br>—OH<br>—OH | + $MeCl_2$<br>+ $2NH_4Cl$ | —O<br>—O—Me—Cl . . . $2NH_4^+$ + 3HCl<br>—O |
| (3) | —OH<br>—OH<br>—OH | + $MeCl_2$<br>+ $2NH_4Cl$ | —O<br>—O—Me—$NH_3$ . . . $NH_4^+$ + 4HCl<br>—O |
| (4) | —OH<br>—OH | + $MeCl_2$<br>+ $2NH_4Cl$ | —O<br>—O Me Cl<br>Cl . . . $2NH_4^+$ + 2HCl |
| (5) | —OH<br>—OH | + $MeCl_2$<br>+ $2NH_4Cl$ | —O<br>—O Me Cl<br>$NH_3$ . . . $NH_4^+$ + 3HCl |
| (6) | —OH<br>—OH | + $MeCl_2$<br>+ $2NH_4Cl$ | —O<br>—O Me $NH_3$<br>$NH_3$ + 4HCl |

were taken into account as the ligands for the adsorbed zinc ion. Because the present experiments were carried out mostly in 2 M $NH_4Cl$ solution.

In equation (1), four —OH groups of the silica surface are acting as an tetradentate ligand. In equations (2) and (3), three groups are acting as an tridentate ligand, and in equations (4), (5) and (6) two groups as a bidentate ligand. In order to keep electrical neutrality at the silica surface with the adsorbed metal ion, one or two $NH_4^+$ ions may be held close to the surface complex. According to these six mechanisms, equations (1)–(6), the possible mole-ratios of $H^+$ released/$Me^{2+}$ adsorbed are 2·0, 3·0 and 4·0.

For the zinc ion adsorption on silica in 2 M $NH_4Cl$, the mole-ratio was 3·0, corresponding to either equation (2) or (5). For zinc ion adsorption on $MnO_2$ in 2 M $NH_4Cl$ the mole-ratio, $H^+$ rel./$Zn^{2+}$ ads., was found to be 2·0 at pH values of the solutions between 4·5 and 6·8.[1,15] For $MnO_2$ only equation (4) can explain the ratio, 2·0, and also the ligands on the solution side must be Cl. From this results on $MnO_2$ and a previous investigation[16] of zinc ion complexes in $NH_4Cl$ solutions, one can

[15] A. KOZAWA, Unpublished work (1960).
[16] T. TAKAHASHI and K. SASAKI, *J. Electrochem. Soc. Japan* **25**, 58 (1957).

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assume that the predominant ligand for zinc ions in 2 M $NH_4Cl$ solution with pH below 6·8 is Cl. Therefore, of the two possibilities for zinc ion adsorption on silica, equation (2) should be preferable; that is, the silica surface is acting as tridentate ligands.

Silica is constructed of tetrahedral silicate ions, which has one Si atom at the centre and four O atoms at the corners of the tetrahedron. Considering that the silica surface probably also has a tetrahedral structure, the tridentate nature of the silica surface may be understood. Also the tridentate nature of the silica surface for zinc ion adsorption may be partly attributed to the nature of zinc ion which forms tetrahedral complexes.

For the $Cu^{2+}$ ion adsorption on the silica surface in 1 M $NH_4Ac$ solution, with pH 6·5, the mole-ratio of $H^+$ rel./$Cu^{2+}$ ads. was 4·0. As Cu ion forms square planar complexes, equation (1) is not impossible. This equation, however, is not likely, since it requires a special distribution of —OH groups on the silica surface as ligands for $Cu^{2+}$ ion and as mentioned above the silica surface seems to act as tridentate ligands. At the present time, it is difficult to decide which equation, (3) or (6), represents $Cu^{2+}$ ion adsorption on the silica surface.

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# RELATIVE RATES OF ALKALINE HYDROLYSIS OF SOME *CIS* AND *TRANS* RING-SUBSTITUTED DIBENZOATO *BIS*(ETHYLENEDIAMINE) COBALT(III) IONS*

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**Abstract**—The rate constants for the alkaline hydrolysis of the first displaced benzoato ligand in some *m*- and *p*-substituted $[Coen_2(OCOC_6H_4X)_2]^+$ ions have been determined in water and aqueous methanol at 25°C by a potentiometric titration method. In the case of the *trans* complexes, the rates depend on the nature of the displaced benzoato ligand and fit the Hammett equation with a low reaction constant, 0·745. The structural effect is less regular in the *cis* series and the rates are probably influenced by the adjacent "non-reacting" benzoato ligand through field and solvent effects. The results are consistent with a dissociative mechanism involving cobalt–oxygen fission.

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THE acid and base hydrolyses of acetato pentammino cobalt(III) ions have been given attention in recent studies[1,2] by both kinetic and $O^{18}$ tracer techniques. We have now started a programme concerning the hydrolysis of acido complexes containing aromatic carboxylato groups as the acido ligands. Preliminary investigations with the $[Co(NH_3)_5OCOC_6H_5]^{2+}$ ion[3] and further unpublished studies with some ring-substituted derivatives have shown that undesired decomposition with loss of ammonia competes with the hydrolysis reaction still more seriously than in the analogous acetato compounds[1] especially in the case of the least reactive derivatives. Consequently, extensive investigations involving changes in structure appeared to be rather a difficult task in that series.

The hydrolysis of dibenzoato *bis*(ethylenediamine) cobalt(III) ions is free from the above complications and, therefore, is a more suitable reaction for extensive correlations of reactivity with structure. In the present paper we report the kinetics of the alkaline hydrolysis in water and aqueous methanol at 25°C of a number of *cis* and *trans* ring-substituted dibenzoato *bis*(ethylenediamine) cobalt(III) complexes. Such complexes offer several points of interest, such as the degree of sensitivity of the reaction to the effects of the structural changes in the benzoato groups, the comparison with the behaviour of organic benzoates, the test of the validity of the Hammett equation and the relationship of *cis* and *trans* configurations to reactivity.

## RESULTS

The hydrolysis of a dibenzoato *bis*(ethylenediamine) cobalt(III) ion proceeds by the following steps:

$$[Coen_2(ArCO_2)_2]^+ + OH^- \xrightarrow{k} [Coen_2(ArCO_2)OH]^+ + ArCO_2^- \quad (1)$$

$$[Coen_2(ArCO_2)OH]^+ + OH^- \xrightarrow{k'} [Coen_2(OH)_2]^+ + ArCO_2^- \quad (2)$$

* Structure and Reactivity in Octahedral Complexes – II.
† To whom correspondence should be addressed.

[1] F. BASOLO, J. G. BERGMANN and R. G. PEARSON, *J. Phys. Chem.* **52**, 22 (1952).
[2] C. A. BUNTON and D. R. LLEWELLYN, *J. Chem. Soc.* 1692 (1953).
[3] G. ILLUMINATI and F. APRILE, *Ricerca Sci.* **28**, 1489 (1958).

In aqueous media, the species thus formed are all basic and tend to equilibrate with the conjugated acids to extents depending on pH. We have not attempted to isolate the intermediate benzoatohydroxo complex produced in reaction (1), but have carried out preparative experiments under conditions close to the ones used for the kinetic measurements in order to identify the products of the over-all reaction (see Experimental). Evidence for the decomposition of the complex other than hydrolysis has never been found under the conditions of the rate experiments.

The reaction rates in either water or aqueous methanol were followed by potentiometric acid-base titrations[3] in experiments with initial concentrations in the region of $10^{-3}$ M in the complex and in the hydroxide ions. This method is sensitive to the buffering effect of the weak conjugated acids formed during the reaction; as the reaction progresses the titration eventually will stop yielding a clean-cut equivalence point. However, in most cases the reaction could be followed up to 50 per cent changes and in one case (dinitrobenzoato derivative) up to 80 per cent change with respect to reaction (1).

Alternative methods to follow the rate of the reaction have also been considered but were not found suitable to our present problem. An isolation method based on extraction of the freed benzoic acid with an organic solvent proved to be valuable only in a semi-quantitative way for the reasons stated in the experimental part; it was therefore used in the preparative experiments intended to ascertain the course of the over-all reaction. A spectral method was also attempted and, although the change in optical density for the benzene ring absorption in the ultra-violet is negligible, the change was found appreciable for the complexed Co(III) absorption in the visible. The main difficulty in applying direct spectrophotometric methods in this region was the lack of the knowledge of the extinction coefficient for the intermediate ion $[Coen_2(OCOAr)OH]^+$ in the consecutive reactions (1) and (2) since this compound has not yet been isolated at this stage of our work.

Treatment of the rate data with the second-order rate law on the assumption of a reaction first order in each reactant, yielded linear plots up to at least 40 per cent with respect to reaction (1) with a drift thereafter as consecutive reaction (2) became important (Fig. 1). From the linear portion of such plots the $k$ values for all the investigated complexes were evaluated.

Due to the low solubility, the initial concentration of the complex was not changed by factors greater than two and the second order rate constants were found to vary within the limits of the experimental error range. This is not considered, however, an exhaustive test for the reaction order. At any rate, in this paper we are primarily concerned with the effects of structural changes on reactivity (free energy of activation). Since what is needed in this case is a set of relative rates under identical experimental conditions, we have computed the second order rate constants from a set of experiments at the same concentration, solvent and temperature for all members of the series considered.

The particularly low solubility in water of some of the compounds of the *trans* series did not allow to carry out the kinetic measurements for the whole group in this solvent. The rate constants in water at 25°C are recorded in the third column of Table 1. It was necessary to complement such data with experiments in another solvent. We considered aqueous methanol and found that the minimum concentration of the alcohol in water able to dissolve the desired amount of the least soluble complex,

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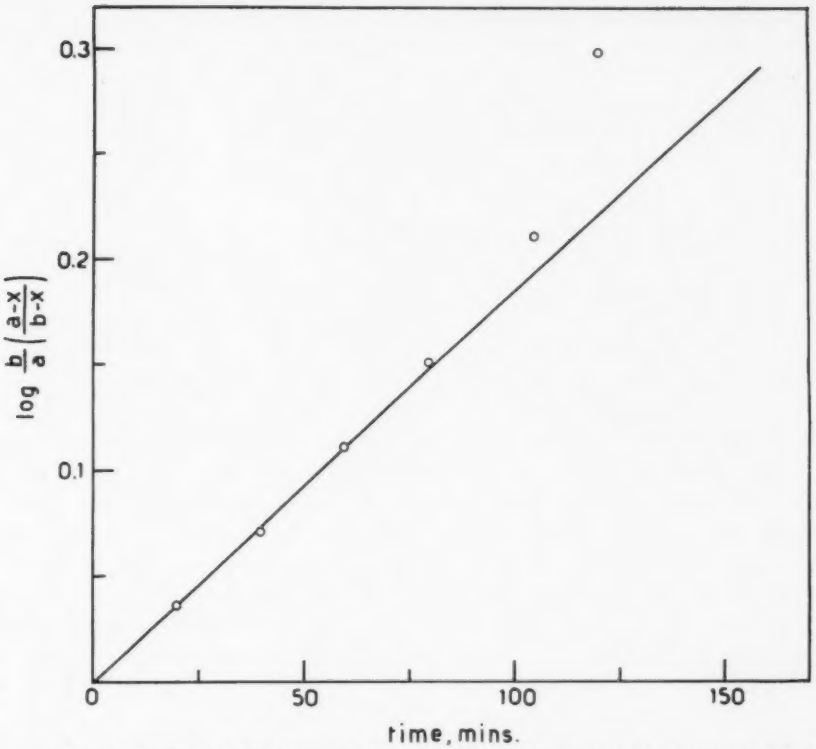



FIG. 1.—Second order plot for the base hydrolysis of *cis*-$(Coen_2(OCOC_6H_4$-*m*-$F)_2)ClO_4$ in water at 25°.

TABLE 1.—SECOND-ORDER RATE CONSTANTS AT 25°C FOR THE ALKALINE HYDROLYSIS OF THE FIRST FUNCTIONAL GROUP IN SOME *cis* AND *trans*-$[Coen_2(OCOC_6H_4X)_2]^+$ IONS*

| X | $\sigma$† | *Cis* Isomers | | *Trans* Isomers | |
|---|---|---|---|---|---|
| | | $10^2 \times k$ (in water) | $10^2 \times k$ (in 40% aq. methanol) | $10^2 \times k$ (in water) | $10^2 \times k$ (in 40% aq. methanol) |
| *p*-$CH_3O$ | −0·268 | 5·18‡ | 3·75 | 2·10 | 1·85 |
| *p*-$CH_3$ | −0·170 | 4·60 | | 2·38** | 2·38 |
| *m*-$CH_3$ | −0·069 | 4·75** | | 2·43 | 2·58 |
| H | 0 | 4·12‡ | 3·17 | 3·20‡ | 3·30 |
| *p*-Cl | 0·227 | 8·38** | | | 4·93 |
| *m*-F | 0·337 | 8·95 | | 5·32** | 5·43 |
| *m*-Cl | 0·373 | 9·77** | | | 5·70 |
| *m*-$NO_2$ | 0·710 | 27·6‡ | 26·3 | | 10·2 |

(*) The *k* values are in $l.mole^{-1}sec^{-1}$ and refer to experiments with initial concentrations $0{\cdot}9 \times 10^{-3}$ M in complex and $1{\cdot}8 \times 10^{-3}$ M in hydroxide ion. The experiments were run in duplicate except when otherwise indicated.

† These values were taken from the recent compilation of McDANIEL and BROWN.[4]

†† Run in triplicate.

** Single run.

the *trans m*-nitro derivative, was 40 per cent by volume. The kinetic form in 40 per cent methanol appeared to be essentially the same as that in water. The rate constants in this solvent at 25°C are recorded in the sixth column of Table 1 for all the *trans* derivatives. Table 1 also includes, for comparison, the rate data for some of the *cis* complexes in aqueous methanol and for some of the *trans* complexes in water.

## DISCUSSION

The substituents in the benzoato ligands were selected in order to cover a broad range of electronic effects, from the strong electron-releasing methoxy to the strong electron-withdrawing nitro group. Nevertheless, as Table 1 shows, the corresponding reactivity range is relatively narrow, the largest increase in rate being only seven fold in the *cis* series and five-fold in the *trans* series. Halogens and the nitro group have all activating influence in both series whereas the expected opposite effect of methyl and *p*-methoxy groups is observed only in the *trans* series.

*Cis*-$[Coen_2(OCOAr)_2]^+$ ions were found to be more reactive than the corresponding *trans* isomers by a factor of 2·5–1·3 in both solvents used, except for the unsubstituted benzoato terms, where the rates of the two isomers in aqueous methanol were practically identical, in fact very slightly inverted. Although the data reported in this paper for the reaction in the mixed solvent were only intended to overcome solubility difficulties (see preceding section) and, therefore, are insufficient for discussion on solvent effects in detail, we may note from Table 1 that methanol has a significant decreasing effect on the rate of the *cis* unsubstituted and methoxy-substituted benzoato terms, but only effects within the experimental uncertainty in the case of the *cis m*-nitro substituted benzoato term and of all investigated *trans* terms.

In the *trans* series the rate data can be correlated with the dissociation constants of the corresponding acids. To illustrate this we have plotted the log $k$'s for the reaction in aqueous methanol vs. Hammett's $\sigma$ constants and obtained a fair linear correlation (Fig. 2). The least-square value for the reaction constant, $\rho$, was found to be 0·745, the correlation coefficient and the standard deviation being 0·911 and 0·061, respectively. There are only few reports on free-energy relationships for reactions in co-ordination chemistry[1,5,6,7] and this appears to be the first typical application of the Hammett equation involving substituted benzoato ligands. The complex ion undergoing reaction (1) contains two identical functional groups, the benzoato ligands, one of which is the "displaced" ligand and the other, *trans* to it, may be referred to as the "non-reacting" ligand. From the above correlation with acid strengths and the low reaction constant it is inferred that the structural effects on rates we are measuring are those of the displaced ligand and that the contribution from the polar effect of the more distant non-reacting ligand is of minor importance. This view is also supported by the previous observation that substituents in N-heteroaromatic "non-reacting" ligands have very small effects on the base hydrolysis rates of $[Coen_2\ py\ Cl]^{2+}$.[8] Yet in the latter complexes polar effects of the substituents in

* Because of an alternative mechanism (carbonyl addition), acyl–oxygen bond fission cannot be established with certainty. For a discussion on this point, see references 2 and 9 (a) and (b).

[4] D. H. MCDANIEL and H. C. BROWN, *J. Org. Chem.* **23**, 420 (1958).
[5] R. W. TAFT, JR., *J. Amer. Chem. Soc.* **75**, 4231 (1953).
[6] P. ELLIS, R. HOGG and R. G. WILKINS, *J. Chem. Soc.* 671 (1959).
[7] W. G. BORDUIN and G .S. HAMMOND, U.S.A.E.C. Report ISC-946 (1957).
[8] F. BASOLO, J. G. BERGMANN, R. E. MECKER and R. G. PEARSON, *J. Amer. Chem. Soc.* **78**, 2676 (1956).

the *py* ligand are relayed to the reaction centre by a substantially shorter path than in a benzoato ligand.

The observed second-order kinetics and the direction of the substituent effects are not diagnostic for the main mechanisms proposed for the base hydrolysis of cobalti-ammino complexes, $S_N2$ and $S_N1CB$.[9] However, the normal behaviour of the *trans* series with regard to structural effects suggests that no change in mechanism occurs along the investigated terms of the series. This and further analysis of the Hammett plot may have a bearing on the problem of what bond is severed in the

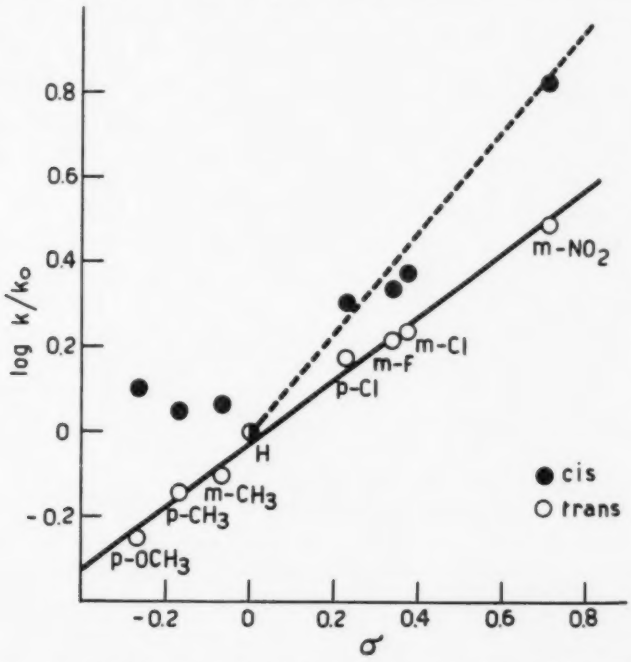
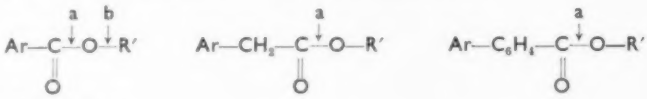



FIG. 2.—Hammett's plot for the base hydrolysis of some *cis*-$[Coen_2(OCOC_6H_4X)_2]^+$ ions in water and of the corresponding *trans*-$[Coen_2(OCOC_6H_4X)_2]^+$ isomers in 40 per cent methanol at 25°.

transition state of the reaction. In $^{18}O$ studies[2] BUNTON has found for the alkaline hydrolysis of the similar ions $[Co(NH_3)_5OCOCR_3]^{2+}$, $CR_3$ being a methyl or a substituted methyl group, that a gradual transition occurs of the cobalt–oxygen over to the acyl–oxygen bond rupture* as the acid strength of the aliphatic acid increases along a series from a $pK_a$ value of 4·7 (acetic acid) up to a value of 0·23 (trifluoroacetic acid). If the reaction mechanism does not change within the present series, decision is only to be made on which bond rupture is involved in all investigated *trans* complex ions. From the acid strength correlation there is a first indication that the cobalt–oxygen bond is the one broken in the removal of the ligand since the acid strength of the benzoic acids herein considered varies in the $pK_a$ range of 4·5 to 3·4, which is much closer to the acetic acid than to the trifluoroacetic acid value. Furthermore in

[9] For extensive surveys on the mechanism of base hydrolysis of octahedral complexes see (a) F. BASOLO and R. G. PEARSON, *Mechanisms of Inorganic Reactions*, J. Wiley, New York (1958); (b) D. R. STRANKS in J. LEWIS and R. G. WILKINS *Modern Co-ordination Chemistry*, Interscience, New York (1960); See, also, R. G. PEARSON, H. H. SCHMIDTKE and F. BASOLO, *J. Amer. Chem. Soc.* **82**, 4434 (1960).

the alkaline hydrolysis of esters, which generally takes place through a $B_{AC}2$ mechanism[10] involving acyl–oxygen fission, Hammett's reaction constants[11] vary in a range from 1·8 to 2·5 in a great number of reactions (Ia):




Bond fission:

Ia ($\rho$ = 1·8–2·5) IIa ($\rho$ = 0·6–0·8) IIIa ($\rho$ = 0·6)

Ib ($\rho$ = 0·7)

Now, the reaction constant, which is a measure of the sensitivity of the reaction centre to any structural changes in Ar, decreases markedly by increasing the distance between the reaction centre and Ar (IIa and IIIa). If in the *trans* dibenzoato complexes acyl–oxygen fission occurred, such complexes would behave as a class of esters with respect to alkaline hydrolysis ($R' = -Coen_2X^+$), and a high value of $\rho$ would be expected for this reaction. The observed value, 0·745, is however in contrast with the sensitivity typical of a reaction involving the acyl–oxygen bond in structures of series I and suggests that the reaction centre is one atom removed from Ar, that is, involves the cobalt–oxygen bond (Ib).

In the *cis*-$[Coen_2(OCOAr_2)]^+$ ions the structural effects on rates are less simply correlated with the acid strengths of the corresponding benzoic acids. In this series the rate data available for all terms are those for the reaction in water. As Table 1 shows, the rates go through a minimum for $\sigma = 0$(hydrogen) when ordered according to increasing $\sigma$ constants, as follows: $p\text{-}CH_3O > p\text{-}CH_3 \simeq m\text{-}CH_3 > H < p\text{-}Cl < m\text{-}F < m\text{-}Cl < m\text{-}NO_2$. The effect of the electron-withdrawing substituents is in the same direction but stronger than that observed in the *trans* series, that is, one which is consistent with the effect of the "displaced ligand" in either $S_N2$ or $S_N1CB$ mechanism. When the *cis* data are compared with the *trans* data the points for all substituents fall *above* the *trans* line. This could simply mean a somewhat higher selectivity for the electron withdrawing substituents, (Fig. 2, dotted line), so that it may not be worth speculating on possibly anomalous behaviour with these substituents. Electron-releasing substituents, however, have an increasing effect on the rate, with respect to hydrogen, that is, in the opposite direction to that predicted from their electronic effects whether a bimolecular attack on acyl carbon or cobalt, or a dissociation mechanism is involved.*

Also, dealing with *cis* isomers it would seem that steric strain between "bulky" benzoato groups is important in the observed rate behaviour. However, molecular models show that *m*- and *p*-substituents can be accommodated in several conformations without any apparent direct steric interaction. The detailed behaviour of the *cis* methoxy- and methyl-substituted benzoato complexes can still arise in a number of ways especially if we consider that the kinetic factors involved are small. In the *cis*

* Since, as in the *trans* series, the rates must be still largely dependent on the effect of the displaced ligand, the series herein investigated should not be confused with the other, $Coen_2AX^+$, where the rates of displacement of a given X are exclusively dependent on the effect of the "non-reacting" ligand A *through cobalt* and where a minimum is also observed in aquation when a proper arrangement of the A's is made.[12] The hypothesis of a change in mechanism in our series would not explain the present facts.

[10] C. K. INGOLD, *Structure and Mechanism in Organic Chemistry*, p. 754. Bell, London (1953).
[11] H. H. JAFFÉ, *Chem. Rev.* **53**, 191 (1953).
[12] C. K. INGOLD, R. S. NYHOLM and M. L. TOBE, *Nature, Lond.* **187**, 477 (1960).

configuration the displaced ligand is close to an identical, non-reacting functional group with varying polarity along the terms of the series so that the polar environment about that displaced ligand is not held constant unlike the *trans* configuration. In the latter two en ligands act as an insulating band between the benzoato ligands, whereas in a *cis* complex the electron-releasing effect of a *p*-$CH_3O$ or $CH_3$ substituents results in increased repulsion between the adjacent carboxylato groups by a polar effect through space (field effect) and/or hindrance to increased solvation of the reacting complex. Both such effects would be consistent with a rate increase in the case of the dissociative mechanism. Finally, a stronger $\pi$-bonding could be another factor acting in the direction of increased rates for the *cis* benzoato complexes containing electron-releasing substituents. However, for a dissociative mechanism involving a conjugated base of a cobalti ammine, the importance and, even, the direction of the effect depends on the structure of the base which at present is not known.

The elucidation of the relative importance of the several factors involved in the behaviour of $[Coen_2(OCOR)_2]^+$ ions requires further investigations in connexion with the structural effects of the ligands, the role of solvation and the rate dependance on temperature. Such studies are now in progress in these laboratories.

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## EXPERIMENTAL

*Materials and apparatus.* The *cis* and *trans* dibenzoato complexes were prepared according to the methods described in the preceding paper. Commercial reagent-grade sodium hydroxide, hydrochloric acid, perchloric acid and absolute methanol were used throughout the work. Distilled water as a reaction medium was freshly boiled and stored in a flask provided with a soda-lime tube.

The potentiometer used was a Beckman model G pH-meter with conventional external glass electrodes. Least-square treatment of the data was carried out by use of an Olivetti computing machine.

*Over-all hydrolysis experiments.* These were carried with *cis* and *trans*-$[Coen_2(OCOC_6H_5)_2]ClO_4$. An alkaline solution (500 ml) 0·004 M in complex and 0·01 M in hydroxide ion was kept in a ground-glass brown bottle at 50° for 16 hr. The solution was then analysed for the benzoic acid set free. A 100 ml sample was made with 50 ml of 0·1 N perchloric acid and extracted with 70 ml portions of diethyl ether. From the ether extract on cautious removal of the solvent, a 95–99 per cent recovery of a benzoic acid residue, m.p. 119°, was obtained and characterized by a mixed m.p. with an authentic specimen, m.p. 121·7°, and by the ultra-violet spectrum. In this procedure, traces of cobalt complexes are extracted together with the acid; also, when the extract is dried over a solid drying agent some of the acid is lost as adsorbed on it. Such features are serious causes of error for a spectrophotometric determination of the acid directly in the extract and prevented an analytical application of the extraction technique in the kinetics of hydrolysis. The impure dihydroxo complex was recovered in form of deep red-purple crystals by direct evaporation in a porcelain dish of a portion of the alkaline reaction solution. The residue was washed with 0·1 M NaOH, 3 M $NaClO_4$, water, alcohol and ether. The cobalt content was found to be 17·83 per cent (calc. for $[Coen_2(OH)_2]ClO_4$: 18·83).

*Rate measurements.* A 250 ml volumetric flask was partially filled with a solution of the calculated amount of complex in the desired solvent and thermally equilibrated in a water thermostat at 25 ± 0·1°C. Where the crystals would dissolve too slowly, magnetic stirring was effected with a calibrated glass-coated magnet. The calcd. volume of a 0·1 N sodium hydroxide solution was then added, the flask filled to the mark with additional solvent and the reaction solution rapidly poured into a glass-stoppered brown bottle immersed in the thermostat. A number of 25 ml samples were withdrawn at convenient time intervals and analysed potentiometrically for residual alkali concentration. Each sample was quenched in an excess of perchloric acid and the resulting solution (about 27 ml) was back titrated with a carbonate free 0·01 N sodium hydroxide solution. This solution was delivered from a microburette and pH measurements were recorded on consecutive 0·10 ml. additions of the reagent. The result is shown in Fig. 3 which reports plots of pH vs. volume of titrating reagent at times 0 and $t$ in the case of the hydrolysis of the *cis* di-*m*-nitrobenzoato complex.

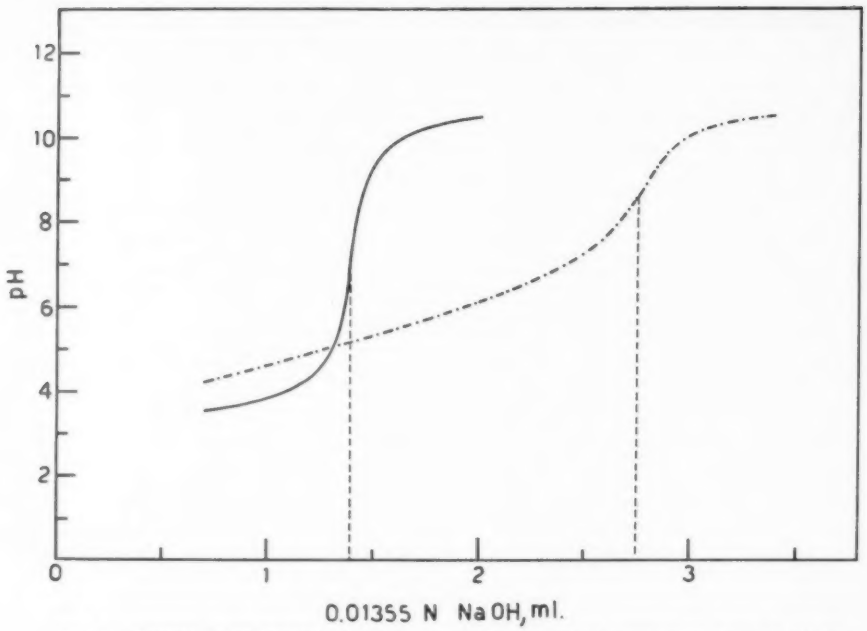


FIG. 3.—Typical potentiometric titration curves for quenched samples at times 0 (solid line) and $t$ (75 per cent reaction) for the base hydrolysis of *cis*-$[Coen_2(OCOC_6H_4\text{-}m\text{-}NO_2)_2]ClO_4$ in water at 25°.

TABLE 2.—TYPICAL KINETIC EXPERIMENTS AT 25°C

| Compounds and conditions | Time (min) | NaOH (ml)* | Reaction (%) | $\text{Log}\frac{b}{a}\left(\frac{a-x}{b-x}\right)^*$ |
|---|---|---|---|---|
| *trans*-$[Coen_2(OCOC_6H_5)_2]ClO_4$ | 0 | 1·40 | 0 | 0 |
| $a = [OH^-] = 1{\cdot}8 \times 10^{-3}$ M | 30 | 1·55 | 9·0 | 0·0210 |
| $b = 9 \times 10^{-4}$ M | 65 | 1·70 | 18·0 | 0·0455 |
| in water | 95 | 1·80 | 24·1 | 0·0639 |
| | 125 | 1·90 | 30·0 | 0·0847 |
| | 155 | 1·98 | 35·0 | 0·1033 |
| | 205 | 2·12 | 41·5 | 0·1350 |
| | 255 | 2·20 | 48·2 | 0·1658 |
| | 305 | 2·35 | 57·0 | 0·2100 |
| *trans*-$[Coen_2(OCOC_6H_4NO_2)_2]OCOC_6H_4NO_2$ | 0 | 2·15 | 0 | 0 |
| $a = [OH^-] = 1{\cdot}8 \times 10^{-3}$ M | 15 | 2·45 | 13·5 | 0·0295 |
| $b = 9 \times 10^{-4}$ M | 30 | 2·70 | 24·6 | 0·0613 |
| in 40% aqueous methanol | 45 | 2·89 | 33·2 | 0·0855 |
| | 60 | 3·05 | 40·0 | 0·1121 |
| | 75 | 3·21 | 47·3 | 0·1433 |

* The values for the reaction in aqueous methanol include blank corrections.

The deformation of the curve for time $t$ with respect to that for time 0 and the shift of the equivalence point to a higher pH are produced by proton equilibration between perchloric acid and the conjugated bases of weak acids formed as reactions (1) and (2) progress. The effect is predicted by the equation.

$$pH = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_a + \tfrac{1}{2}\log C,$$

where $C$ and $pK_a$ are the concentration and $pK$ of the acid to be titrated, since pH at the equivalence point increases as $pK_a$ increases. Nevertheless, the total acid concentration remains unchanged and is measured, as usual, by the shift of the equivalence point along the abscissa. Equivalence points were detected graphically by the differential method. A typical kinetic run in water is reported in Table 2.

Blank experiments showed that repeated sampling and analysis of a 5 hr kinetic run according to the procedure described above are affected by atmospheric $CO_2$ but negligibly. Also blank runs were set up to ascertain the stability of the solutions of *cis* and *trans* dibenzoato complexes during the reaction time.

Absorption spectra showed only 2 per cent change in optical density in the case of *cis*-$[Coen_2(OCOC_6H_5)]_2^+$ at 25° in water whereas the *trans* isomer remained unchanged in a 4 hr time. Stability is higher still in methanol solution at the same temperature.

In the experiments carried out in aqueous methanol, different stocks of commercial alcohol were found to use up varying amounts of hydroxide ion. Blank runs paralleled such experiments to bring a correction at any desired time to the titration value. A typical kinetic run in aqueous methanol is reported in Table 2.

*Evaluation of the data.* The calculation of the rate constants was based upon the equation: $\log b(a-x)/a(b-x) = (a-b)kt + C$, in which $a$ and $b$ are the concentrations of the reactants at the zero time of the reaction and $x$ the concentration of the product formed at time $t$. The slopes of the initial linear portion of the plot $\log b(a-x)/a(b-x)$ vs. $t$ and of the plot $\log k/k_0$ vs. Hammett's constants were calculated by the method of least squares. The probable errors in the $k$ values taken as the mean percentage deviation from the mean in duplicate runs did not exceed 10 per cent.

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# THE EXTRACTION OF THORIUM FROM NITRATE SOLUTION BY DIBUTYL BUTYL PHOSPHONATE

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**Abstract**—Thorium nitrate is more readily extracted by dibutyl butyl phosphonate (DBP) than by tri-*n*-butyl phosphate (TBP). It is extracted as a tri-solvate and the reaction may be represented by the equation

$$Th(NO_3)^{3+} + 3NO_3' + 3DBP = Th(NO_3)_4 \cdot 3DBP$$

The distribution of thorium to the organic phase is approximately halved when nitrobenzene is substituted for kerosene as a solvent for the reagent, but in either case the reaction is represented by the equation given.

IN the course of examining organophosphorus compounds for their ability to extract metals from aqueous solutions we found that dibutyl butyl phosphonate (DBP) was an effective extractant for thorium nitrate. HESFORD *et al.*[1] have shown that thorium nitrate is quite strongly extracted by tri-butyl phosphate (TBP), but it is even more strongly extracted by DBP, which gives a higher distribution into the organic phase at lower concentration of nitrate in the aqueous phase, and also at lower concentration of reagent in the organic phase. Since of the neutral reagents examined DBP showed the most promise as an extractant for thorium, the factors governing the extraction were investigated in some detail, particularly with a view to elucidating the chemistry of the process.

## EXPERIMENTAL

The sample of dibutyl butyl phosphonate was supplied by Albright and Wilson Ltd. It had a refractive index $n_D^{25} = 1{\cdot}4300$ (the value recorded by KOSOLAPOFF[2] is 1·4302) and was used as received. As solvents for the reagent twice-distilled Shell lighting kerosene (boiling range 185–235°C) and pure nitrobenzene were used, the latter being chosen on account of its high dielectric constant. Aqueous and organic phases were equilibrated by stirring at 25·0°C for 1 hr. Equal volumes (20·0 ml) of each phase were used, except in the case of pure thorium nitrate solutions, when 5·0 ml of aqueous were contacted with 50·0 ml of organic solution. After phase disengagement the separated phases were filtered and thorium was determined in each phase by X-ray fluorescence analysis.

The nitrate concentration of the aqueous solutions was adjusted to the required value by the addition of potassium nitrate. No nitric acid was added, except in one series of experiments, when small amounts were added to reduce the pH of the original solution from 3·10 to 1·90. The solutions of pure thorium nitrate, free from potassium nitrate, were made up of known molality, and the concentration of thorium nitrate was determined by analysis.

Conductivity measurements were made with a Philips conductivity bridge. The readings were corrected by subtracting the blank value obtained under the same conditions but with no thorium present in the aqueous phase.

[1] E. HESFORD, H. A. C. MCKAY and D. SCARGILL, *J. Inorg. Nucl. Chem.* **4**, 321 (1957).
[2] G. M. KOSOLAPOFF, *Organophosphorus Compounds*, p. 150. J. Wiley, New York (1950).

## RESULTS AND DISCUSSION

Table 1 shows the results of extracting a 0·0107 M thorium nitrate solution, adjusted to a total nitrate concentration of 2 M, with kerosene solutions of DBP of various concentrations. The extractions were make at two pH levels. The first, 3·10, was the natural pH of the thorium nitrate–potassium nitrate solution; the second, 1·90,

TABLE 1.—EXTRACTION OF THORIUM AT CONSTANT (2 M) NITRATE CONCENTRATION

| DBP in kerosene (mole/l.) | Distribution ratio (organic:aqueous) | | | | | |
|---|---|---|---|---|---|---|
| | 0·05 | 0·10 | 0·20 | 0·30 | 0·40 | 0·50 |
| pH 3·10 | 0·040 | 0·240 | 1·62 | 5·22 | 13·2 | 25·1 |
| pH 1·90 | | 0·279 | 1·92 | 5·79 | 13·6 | |

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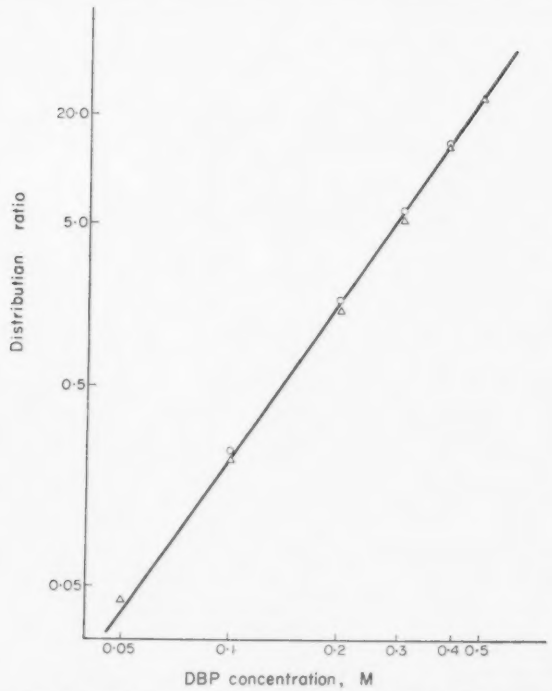


FIG. 1.—Distribution of thorium as a function of DBP concentration.
△ pH 3·10
○ pH 1·90

was obtained by adding nitric acid to the first solution, thus slightly increasing the total nitrate concentration, which accounts for the slightly greater distribution ratios found. A log–log plot of distribution ratio against DBP concentration is shown in Fig. 1. The line has a slope of 2·9, indicating the formation of tri-solvate, $Th(NO_3)_4 \cdot 3DBP$. HESFORD *et al.*[1] obtained results implying a cube law for the extraction of thorium nitrate with TBP under certain conditions, and, as they point out, others have postulated such compounds. But they did not consider the evidence for a tri-solvate

sufficiently strong, and preferred to adhere to the conclusion that only a di-solvate is formed with TBP. However, the formation of a tri-solvate with DBP, which seems established by the present evidence, suggests the possibility of the existence of analogous compounds with phosphoric acid esters.

The extraction of thorium may now be represented by the equation

$$Th(NO_3)_n^{(4-n)+} + (4 - n)\,NO_3' + 3DBP = Th\,(NO_3)_4{\cdot}3DBP \qquad (1)$$

If it is assumed that at equilibrium the concentration of the ion $Th(NO_3)_n^{(4-n)+}$ is directly proportional to the total concentration of thorium in the aqueous phase, an equilibrium constant $K_1$ may be written for (1) as follows:

$$K_1 = \frac{D}{(y_{Th(NO_3)_n^{(4-n)+}} \cdot c_{NO_3'}^{4-n} \cdot y_{NO_3'}^{4-n})_w (c_{DBP}^3)_o} \times \frac{(y_{Th(NO_3)_4{\cdot}3DBP})_o}{(y_{DBP}^3)_o} \qquad (2)$$

where $D$ = distribution ratio of thorium (i.e. the ratio of the concentration of thorium in the organic phase to that in the aqueous phase)

$y$ = molar activity coefficient

$c$ = concentration (moles per litre)

and the suffixes $o$, $w$ refer to the organic and aqueous phases respectively. Neglecting the activity coefficients in the organic phase, and assuming that

$$y_{\pm} = (y_{Th(NO_3)_n^{(4-n)+}} \cdot y_{NO_3'}^{4-n})^{1/(5-n)} \qquad (3)$$

where $y\pm$ is the mean molar activity coefficient of thorium nitrate, (2) becomes

$$K_2 = \frac{D}{(y_{\pm}^{5-n} \cdot c_{NO_3'}^{4-n})_w (c_{DBP}^3)_0} \qquad (4)$$

To determine the value of $n$, pure solutions of thorium nitrate were extracted with 0·3 M DBP in kerosene. The results are shown in Table 2. The mean molar activity coefficients of thorium nitrate were calculated from the corresponding molal values taken from ROBINSON and STOKES[3]. If in the expression for $K_2$ the total stoicheiometric nitrate concentration is substituted for the actual nitrate ion concentration, a

TABLE 2.—EXTRACTION OF THORIUM NITRATE FROM PURE AQUEOUS SOLUTION WITH 0·3 M DBP IN KEROSENE

| Thorium nitrate solution before contact | Molality | 0·126 | 0·253 | 0·379 | 0·505 | 0·758 |
|---|---|---|---|---|---|---|
| | Moles/l. | 0·116 | 0·233 | 0·350 | 0·460 | 0·663 |
| Distribution ratio | | 0·0883 | 0·131 | 0·163 | 0·177 | 0·180 |

TABLE 3.—VALUES OF $K_2'$

| $n = 0$ | $n = 1$ | $n = 2$ | $n = 3$ | $n = 4$ |
|---|---|---|---|---|
| $2{\cdot}23 \times 10^5$ | $1{\cdot}89 \times 10^4$ | $1{\cdot}60 \times 10^3$ | $1{\cdot}36 \times 10^2$ | $1{\cdot}16 \times 10$ |
| $1{\cdot}29 \times 10^5$ | $1{\cdot}53 \times 10^4$ | $1{\cdot}82 \times 10^3$ | $2{\cdot}15 \times 10^2$ | $2{\cdot}54 \times 10$ |
| $1{\cdot}17 \times 10^5$ | $1{\cdot}63 \times 10^4$ | $2{\cdot}29 \times 10^3$ | $3{\cdot}21 \times 10^2$ | $4{\cdot}50 \times 10$ |
| $0{\cdot}93 \times 10^5$ | $1{\cdot}56 \times 10^4$ | $2{\cdot}64 \times 10^3$ | $4{\cdot}45 \times 10^2$ | $7{\cdot}51 \times 10$ |
| $0{\cdot}70 \times 10^5$ | $1{\cdot}53 \times 10^4$ | $3{\cdot}36 \times 10^3$ | $7{\cdot}34 \times 10^2$ | $16{\cdot}1 \times 10$ |

[3] R. A. ROBINSON and R. H. STOKES, *Electrolytic Solutions* (2nd Ed.) Butterworths, London (1960).

TABLE 4.—EXTRACTION OF THORIUM WITH 0·3 M DBP IN KEROSENE AT VARYING NITRATE CONCENTRATION

| Nitrate conc. (mole/l.) | 0·5 | 1·0 | 1·5 | 2·0 | 2·5 | 3·0 |
|---|---|---|---|---|---|---|
| Distribution ratio | 0·540 | 2·02 | 3·70 | 5·51 | 7·84 | 9·66 |

constant $K_2'$ is obtained, and values of this, calculated for all values of $n$ between 0 and 4, are shown in Table 3. It is clear from Table 3 that $n$ must be given the value one, and hence the extraction of thorium may be represented by

$$Th(NO_3)^{3+} + 3NO_3' + 3DBP = Th(NO_3)_4 \cdot 3DBP \qquad (5)$$

The results given in Table 3 do not of course imply that $Th(NO_3)^{3+}$ is the only thorium species present in the aqueous phase, or even that it is the predominant species, but they do indicate that it is the species that reacts to form the complex with DBP. The various thorium species in the aqueous phase are in equilibrium, and as one species is removed by reaction, it will be re-formed to restore the equilibrium. It follows that the distribution ratio should vary with the cube of the nitrate ion activity, and an attempt was made to check this by extracting thorium from solutions of fixed (0·01 M) thorium and varying nitrate concentration with 0·3 M DBP in kerosene. The results are shown in Table 4. Neglecting the activity coefficients in the organic phase, and the activity coefficient of the thorium ion in the aqueous phase, and making the assumption that the activity coefficient of the nitrate ion is equal to the mean molar activity coefficient of potassium nitrate ($y\pm$) at the same molarity in pure solution in water, (2) becomes

$$K_3 = \frac{D}{(c_{NO_3'} y_\pm)_w^3 (c_{DBP}^3)_o} \qquad (6)$$

It follows from (6) that a log–log plot of $D/(c_{DBP}^3)_0$ against $(c_{NO_3'} y\pm)_w$ should give a straight line of slope 3. Such a plot is shown in Fig. 2. It gives a straight line of slope

TABLE 5.—EXTRACTION OF THORIUM WITH DBP AND TBP IN NITROBENZENE

| Nitrate in aqueous phase before contact, (mole/l.) | Distribution ratio | | Equivalent conductivity* | |
|---|---|---|---|---|
| | DBP | TBP | DBP | TBP |
| 0·5 | 0·272 | 0·122 | 0·721 | 0·362 |
| 1·0 | 0·895 | 0·358 | 0·591 | 0·220 |
| 1·5 | 1·79 | 0·500 | 0·554 | 0·193 |
| 2·0 | 2·52 | 0·530 | 0·523 | 0·172 |
| 2·5 | 3·54 | | 0·507 | |

* Equivalent conductivity = specific conductivity divided by the concentration of thorium in equivalents per ml.

2·8. Considering the assumptions made in (6), this is in reasonable agreement with (5).

A direct comparison of DBP and TBP was made using nitrobenzene as solvent. The concentration of DBP and TBP in the organic phase was 0·3 M, and that of



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thorium in the aqueous phase before contact was 0·01 M. The results are given in Table 5, which also shows the equivalent conductivity of the thorium complex in the organic phase (that is, the specific conductivity of the solution divided by the concentration of thorium in equivalents per ml.) The limiting value of the equivalent conductivity of electrolytes in nitrobenzene is, by Walden's rule, about thirty, so that, on this

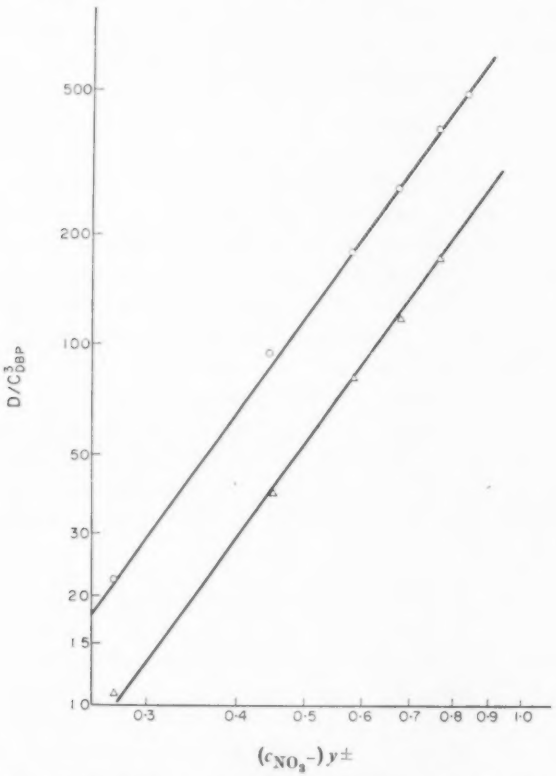


FIG. 2.—Distribution of thorium as a function of nitrate concentration.
○ 0·3 M DBP in kerosene
△ 0·3 M DBP in nitrobenzene

basis, the degree of dissociation is only about 1 per cent for the TBP and 2 per cent for the DBP complex. It may be concluded that these complexes are virtually undissociated in the organic phase.

A comparison of Tables 4 and 5 shows that when kerosene is replaced by nitrobenzene as a solvent for DBP, the distribution ratio of thorium is approximately halved. However, the reaction still follows the same course, as can be seen from Fig. 2, which shows a log–log plot of $D/(c^3_{DBP})_o$ against $(c_{NO_3^-}.y\pm)_w$ for the nitrobenzene extraction. The result is, as before with kerosene, a straight line of slope 2·8.

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# EXTRACTION OF GROUP VIII METALS BY LONG CHAIN ALKYL AMINES—III

## LIQUID ION-EXCHANGE BEHAVIOUR OF THE OXALATE COMPLEXES OF IRON, COBALT AND NICKEL*

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(*Received* 2 *March* 1961; *in revised form* 3 *April* 1961)

**Abstract**—Oxalate complexes of Fe(III), Co(III), Ni(II) and Co(II) have been investigated with respect to their extractability by solutions of long chain alkyl amines in chloroform. Extraction was enhanced by pretreating the amines with acids. The nature of the pretreating acid as well as the structure of the amine were found to affect the extraction efficiency. The results of the investigation lend support to the conclusion that the metallic anions involved in the extraction process are the trioxalato and dioxalato complexes, and that the mechanism of the extraction process is compatible with ion exchange behaviour.

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THE extraction of chloride complexes of Fe(III) and Co(II) by long chain alkyl amines has been previously reported[1,2] with specific attention given to the extraction mechanism and to the identification of the extracted species. In an attempt to elucidate the extraction mechanism of other metal anionic complexes, the investigation has been extended to include oxalate complexes of Co(III), Fe(III), Co(II) and Ni(II). The trioxalato complexes are well characterized in the literature.[3–6] The dioxalato complexes, although less well characterized are reported[3,7] to be less stable than the trioxalato complexes. In this paper, the extraction of trioxalatoferriate (III), trioxalato cobaltate (III), dioxalato cobaltate (II) and dioxalato nickelate (II) by long chain alkyl amines in chloroform solutions is reported.

## EXPERIMENTAL

### *Materials*

A. *Preparation of complex oxalates*

1. $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$. This compound was prepared by a method reported by BAILAR and JONES.[8] An aliquiot of $^{59}Fe$ was added with the ferric sulphate to obtain the labelled compound. The resulting green crystals were dried in a desiccator for several days and then analysed for oxalate and Fe(III) with standard $KMnO_4$. The material was found to lose all water of hydration upon standing in the desiccator. The resulting anhydrous $K_3[Fe(C_2O_4)_3]$ has theoretically 60·38 per cent oxalate and 12·77% Fe. Values found experimentally were: oxalate, 60·23%; Fe, 12·02%.

2. $K_3[C_2O_4)_3]\cdot 3H_2O$. This compound was prepared by a procedure similar to the one for the iron compound above.[8] The compound was labelled with $^{58}Co$ by adding an aliquiot of the isotope to the

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(1) M. L. Good and S. E. BRYAN, *J. Amer. Soc.* **82** 5636 (1960).
(2) M. L. GOOD and S. E. BRYAN, *J. Inorg. Nucl. Chem.* In press.
(3) D. P. GRADDON, *J. Inorg. Nucl. Chem.* **3**, 308, (1956).
(4) J. J. LINGANE, *J. Amer. Chem. Soc.* **68**, 2448, (1946).
(5) C. SCHAAP, H. A. LAITINEN and J. BAILAR, *J. Amer. Chem. Soc.* **76**, 5868 (1954).
(6) V. F. TOROPONA, *J. Gen. Chem. U.S.S.R.* **11**, 1211 (1941).
(7) N. V. SIDGWICK, *The Chemical Elements and their Compounds*, Vol. 2. p. 1447 and p. 1388. Oxford University Press (1950).
(8) H. S. BOOTH (Editor) *Inorganic Synthesis* Vol. 1, p.36. McGraw-Hill, New York (1939).

first step in the preparation. The resulting deep green crystals were dried in the desiccator for several days. The material was analysed by adding excess standard $Ce^{4+}$ solution to a sample of the complex dissolved in $H_2SO_4$. The excess $Ce^{4+}$ was titrated with standard $Fe^{2+}$ solution. Equivalent weight of the complex was mol. wt./5 since the Co(III) was reduced to Co(II). Theoretically, equivalent weight of $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ is 98·8 and per cent Co is 11·93. Experimental equivalent weight was 97·6 and per cent Co was 12·1.

3. $K_2[Ni(C_2O_4)_2]\cdot 6H_2O$. A solution containing this complex was made by dissolving solid $NiC_2O_4$ in a solution containing excess $K_2C_2O_4$. Attempts to recover the solid complex resulted in an apparent double salt. The solutions were standardized with respect to Ni by either precipitating with dimethylglyoxime or by electrodeposition. The spectra of the solution (in excess $K_2C_2O_4$) showed no evidence of the $Ni^{2+}$ ion, so apparently the Ni was essentially all present as the complex.

4. $Na_2[Co(C_2O_4)_2]\cdot 6H_2O$. The compound was prepared by dissolving $^{58}Co$ labelled $CoC_2O_4$ in a solution containing excess $Na_2C_2O_4$. The resulting pink crystals of the complex were dissolved in excess $Na_2C_2O_4$ and the solution analysed by determining the oxalate of the complex with $KMnO_4$ (oxalate of complex being equal to total oxalate minus oxalate in solution used to dissovle complex crystals). For a solution made up to be 0·0250 M a value of 0·0251 M was found experimentally.

B. *Amines and other chemicals*

1. XE–204. Commercial mixture of branched chain tertiary amines from Rohm and Haas Co. Average mol. wt. 406.

2. *Tri-n-hexyl amine*. Straight chain tertiary amine obtained as White Label grade from Eastman Kodak Chemical Co. Mol. wt. 269.

3. *2,2′diethyldihexyl amine*. Branched chain secondary amine obtained as technical grade from Eastman Chemical Co. Mol. wt. 241.

4. LA–2. Highly branched chain secondary amine obtained as a commercial mixture from Rohm and Haas. Average mol. wt. 374.

5. *Primene* 81–R. Branched chain (tertiary carbon) primary amine obtained as a commercial mixture from Rohm and Haas. Average mol. wt. 199.

6. *Organic solvents*. All were analysed, reagent grade materials.

7. *Inorganic compounds*. All were analysed, reagent grade materials.

*Procedure*

Aqueous solutions of the labelled potassium salt of trioxalato ferriate(III), trioxalato cobaltate(III) and dioxalato cobaltate (II) were equilibrated with equal volumes of amine solutions in chloroform. After the two phase system was shaken mechanically for approximately 5 min equal aliquiots of each phase were removed and counted as liquid samples in a well type scintillation counter. The per cent extraction was calculated as:

$$\text{extraction (\%)} = \frac{\text{activity in org. phase}}{\text{activity in the org. and aq. phase}}$$

Time studies on several systems indicated that complete equilibration was obtained after about three minutes of shaking time.

Since there was no appropriate isotope for nickel, the spectrum of dioxalato nickelate (II) was determined. A Beers' law curve was constructed at 670 mμ using the standardized dioxalato nickelate (II) solution and the per cent extraction was obtained by spectrophotometric methods.

The absorption spectra determined were obtained on a Beckman DK–1 spectrophotometer and in those cases where concentrations or extinction coefficients were obtained, a Beckman Model DU spectrophotometer was used.

## RESULTS AND DISCUSSION

### *Oxalate complexes of* Fe(III) *and* Co(III)

The free base amines were found to extract the trioxalato complexes only slightly. However, pretreating the amines with various acids enhanced the extraction. As is shown in Table 1, the nature of the pretreating acid as well as the structure of the amine affect the extraction efficiency. Primene 81-R appeared to be the best extractant

TABLE 1.—PER CENT EXTRACTION OF $M(C_2O_4)_3^{3-}$ BY ALKYL AMINES

| Amine[a]-$M(C_2O_4)_3^{3-}$ [b] | | Free base | Pretreating acids[c] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $HNO_3$ | $HClO_4$ | HCl | $HC_2H_3O_2$ | $H_2C_2O_4$ | $H_3PO_4$ | $H_2SO_4$ |
| XE-204 | Fe(III) | 5·9 | 48·8 | 59·1 | 96·4 | [d] | 100·0 | 95·0 | 96·7 |
| | Co(III) | 19·4 | 43·4 | 63·6 | 92·8 | 89·6 | 93·0 | 88·0 | 87·6 |
| Tri-*n*-hexyl | Fe(III) | 5·9 | 39·9 | 56·6 | 99·0 | 99·0 | 100·0 | 100·0 | 100·0 |
| | Co(III) | 19·6 | 23·8 | 26·2 | 81·2 | 69·9 | 93·5 | 97·4 | 97·7 |
| 2,2′Diethyl-dihexyl | Fe(III) | 9·1 | 55·6 | 83·7 | 98·4 | 97·9 | [e] | 93·1 | 98·8 |
| | Co(III) | 3·6 | 38·7 | 72·3 | 88·9 | 86·7 | [e] | 64·4 | 90·3 |
| LA-2 | Fe(III) | 7·6 | 43·4 | 53·2 | 87·4 | [d] | 100 | — | 97·2 |
| | Co(III) | 4·1 | 35·4 | 51·6 | 85·9 | 86·9 | 91·1 | 89·9 | 96·1 |
| Primene 81-R | Fe(III) | 32·5 | 94·3 | 95·0 | 96·4 | 99·2 | 99·1 | [d] | 94·0 |
| | Co(III) | 0·2 | 90·7 | 93·6 | 90·3 | 93·1 | 97·9 | 0·0 | 89·9 |

[a] All amines were 0·2 M in $CHCl_3$
[b] The concentration of the $M(C_2O_4)_3^{3-}$ was 0·017 M
[c] 3N acid was used to pretreat the amine $CHCl_3$ solution (a saturated solution of $H_2C_2O_4$ was used).
[d] An emulsion formed between the amine solution and pretreating acid.
[e] A precipitate formed between the amine solution and pretreating acid.

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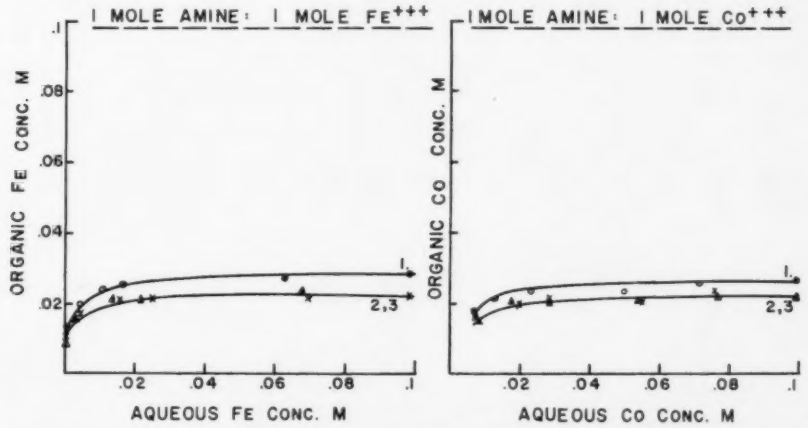


FIG. 1.—Extraction Isotherms for the Extraction of $M(C_2O_4)_3^{3-}$ by HCl-pretreated amines in $CHCl_3$. Curves 1, Primene 81-R; Curves 2, 2,2′diethyldihexyl; Curves 3, tri-*n*-hexyl.

showing little preference for specific anions. Both secondary and tertiary amines showed an order of preference for anions of $NO_3^- > ClO_4^- > Cl^-$ with no difference in preference shown for $C_2H_3O_2^-$, $C_2O_4^{2-}$, $PO_4^{3-}$, and $SO_4^{2-}$. It was possible to strip the Fe(III) oxalate and Co(III) oxalate complexes from the amine solutions with nitric acid, hydrochloric acid and perchloric acid, but not with sulphuric acid.

Extraction isotherms were made in an attempt to determine the stoichiometry of the extracting species. In Fig. 1, loading curves are shown in which 0·1 M amine solutions pretreated with hydrochloric acid are used to extract the metal oxalate complex of varying concentrations. In Fig. 2, similar curves are shown for amine solutions pretreated with sulphuric acid. The limiting mole ratio of amine to metal oxalate complex appears to be 3:1 in all cases. These curves substantiate the extraction data in Table I showing that sulphuric acid is a more effective pretreating

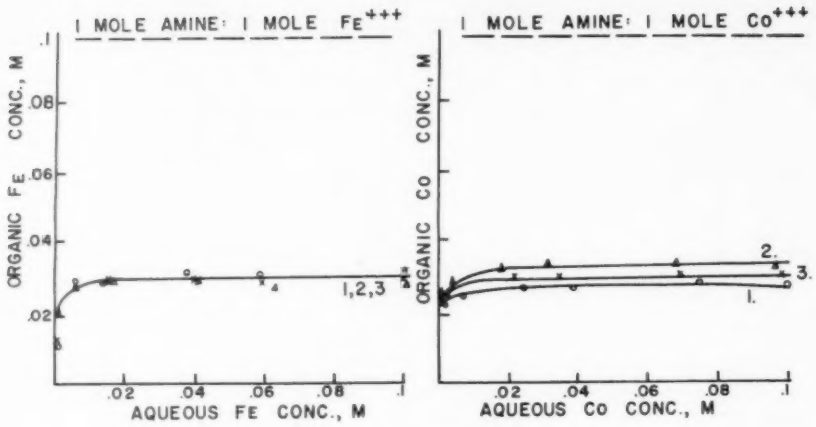


FIG. 2.—Extraction isotherms for the extraction of $M(C_2O_4)_3^{3-}$ by $H_2SO_4$-pretreated amines in $CHCl_3$. Curves 1, Primene 81-R; Curves 2, 2,2′diethyldihexyl; Curves 3, tri-*n*-hexyl.

acid than hydrochloric acid, although Primene 81-R is a better extractant when pretreated with hydrochloric acid. In Fig. 3, loading curves are shown in which the concentration of the metal oxalate complex is constant while the concentration of the amine (pretreated with sulphuric acid) is varied. The ratio of the metal extracted into the organic layer to concentration of amine is plotted against the amine concentration. Again, the curves for tertiary and secondary amines suggest a 3:1 ratio of amine to metal oxalate complex while the curves for Primene 81-R are quite different, exhibiting

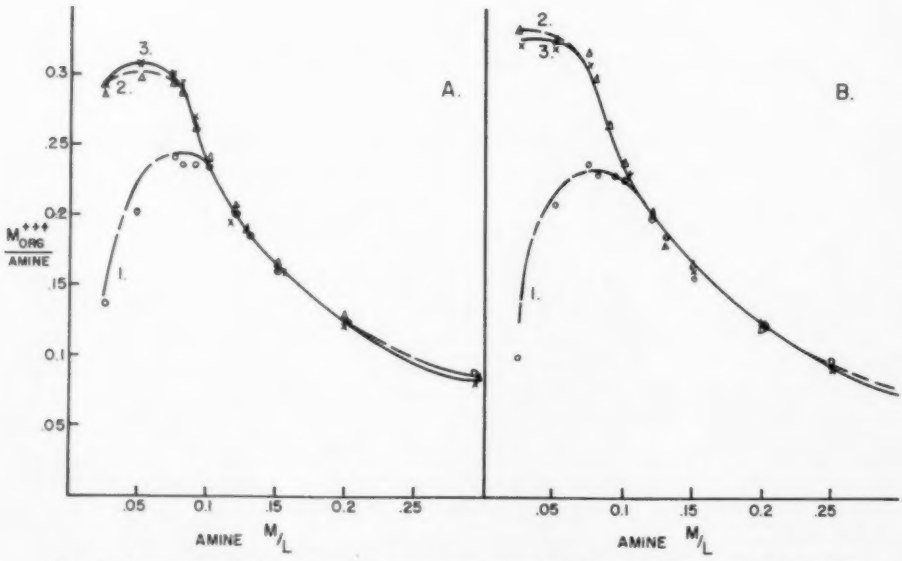


FIG. 3.—Extraction isotherms (variable amine concentration) for the extraction of $M(C_2O_4)_3^{3-}$ by $H_2SO_4$-pretreated amines in $CHCl_3$. Graphs *A*, $Fe(C_2O_4)_3^{3-}$; Graphs *B*, $Co(C_2O_4)_3$. Curves 1, primene 81-R; Curves 2, 2,2′diethyldihexyl; Curves 3, tri-*n*-hexyl.

a maximum. It has been shown[9,10] that sulphuric acid pretreated amines polymerize in solution forming aggregates and that branched chain primary amines form larger aggregates than branched chain secondary or tertiary amines. This phenomenon could explain the appearance of the maximum in the loading curves since aggregation of the amine molecules at low concentrations could decrease the loading efficiency.

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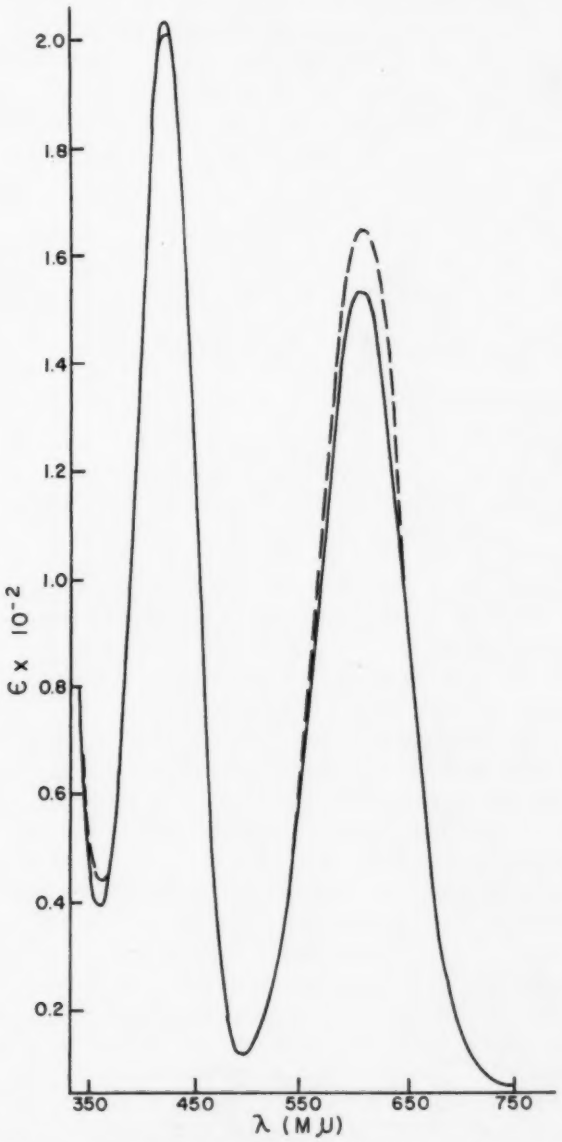


FIG. 4 —Absorption spectra of $Co(C_2O_4)_3^{3-}$ Curve——, aqueous solution; Curve – – – – – extracted species in $H_2SO_4$-pretreated tri-*n*-hexyl amine in $CHCl_3$.

[9] W. J. McDOWELL and K. A. ALLEN, *J. Phys. Chem.* **63**, 747 (1959).
[10] K. A. ALLEN, *J. Phys. Chem.* **62**, 1119 (1958).

Aqueous solutions of trioxalato cobaltate (III) have absorption maxima reported[11] at 600 m$\mu$, 420 m$\mu$ and 260 m$\mu$ which is analogous to the spectra obtained in this study. The visible spectrum of an aqueous solution of the Co(III) oxalate complex is shown in Fig. 4. The ultra-violet peak at 260 m$\mu$ was also observed and an approximate value of $2{\cdot}5 \times 10^4$ was obtained for the molar extinction coefficient. Also shown in Fig. 4 is the spectrum of the extracted species for Primene 81-R pretreated with sulphuric acid. It is obvious that the spectrum of the extracted species is identical to that of the aqueous trioxalato cobaltate (III). Thus it appears that the metallic anion involved in the extraction process is the $Co(C_2O_4)_3^{3-}$ species.

The reported[11] absorption maximum for aqueous solutions of trioxalato ferriate (III) in the visible region is at 650 m$\mu$ which is in agreement with the spectrum shown in Fig. 5. Again the spectrum of the extracted species shown in Fig. 5 is completely analogous to the aqueous spectrum for the Fe(III) oxalate complex and it is evident that the extracted species is the trioxalato ferriate (III) complex ion.

All of the evidence presented above indicates an ion exchange mechanism for the extraction process which might be represented by the following equation:

$$3R_3NH^+ A^- + M(C_2O_4)_3^{3-} \rightleftharpoons (R_3NH^+)_3[M(C_2O_4)_3^{3-}] + 3A^-$$

*Oxalate complexes of* Ni(II) *and* Co(II)

The dioxalato complexes are less efficiently extracted than the trioxalato complexes as is shown in Table 2. Here again the free base amines do not extract the oxalate complex. Primene 81-R showed appreciable enhancement of extraction if pretreated with various acids. The secondary and tertiary amines studied showed an increase in extraction with sulphuric acid pretreat only (and this was less than 30 per cent). In the case Primene 81-R, the order of preference for specific anions is: $NO_3^- > ClO_4^- > Cl^- > C_2H_2O_2^- > C_2O_4^{2-} > SO_4^{2-}$, however differences in extraction values in this system are very small with the exception of those for the sulphuric acid pretreat. It is interesting to note that the trends shown for both dioxalato and trioxalato complexes with respect to preference of anions is analogous to previously reported[13] ion exchange resin studies with the exception of the reverse order of $NO_3^-$ and $ClO_4^-$.

Since the extraction efficiency of the dioxalate complexes is poor, no attempt was made to determine the metal (II)–amine mole ratio.

In Fig. 6, the spectrum of an aqueous solution of dioxalato nickelate (II) is shown. Absorption maxima are found at 375 m$\mu$, 670 m$\mu$ and 1125 m$\mu$. Also shown in Fig. 6 is the spectrum of aqueous nickel nitrate which is completely analogous to that reported for the Ni(II) ion.[13] The spectrum of the dioxalato cobaltate (II) ion was found to have a single absorption peak with a maximum at 530 m$\mu$ in the visible region. This peak shifted slightly as the concentration of excess oxalate in the solution was changed. At slight excess oxalate concentrations the spectrum resembled that of the aqueous Co(II) ion, indicating the instability of the cobalt (II) oxalate complex in aqueous solution. Spectra of the extracted species of both the nickel (II) and the cobalt (II) oxalate complexes were found to be identical to those of the ions in aqueous solution containing excess oxalate ions. Thus, again it appears

[11] N. A. BISIKALOVA, *Ukrain. J. Chim.* **17**, 804–14 (1951); *Chem. Abstr.* **49**, 6734 (1955).
[12] C. F. COLEMAN, K. B. BROWN, J. G. MOORE and K. A. ALLEN, *Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy*, Geneva, 1958. Paper No. 518, United Nations (1959).
[13] R. BASTIAN, *Anal. Chem.* **23**, 580 (1951).

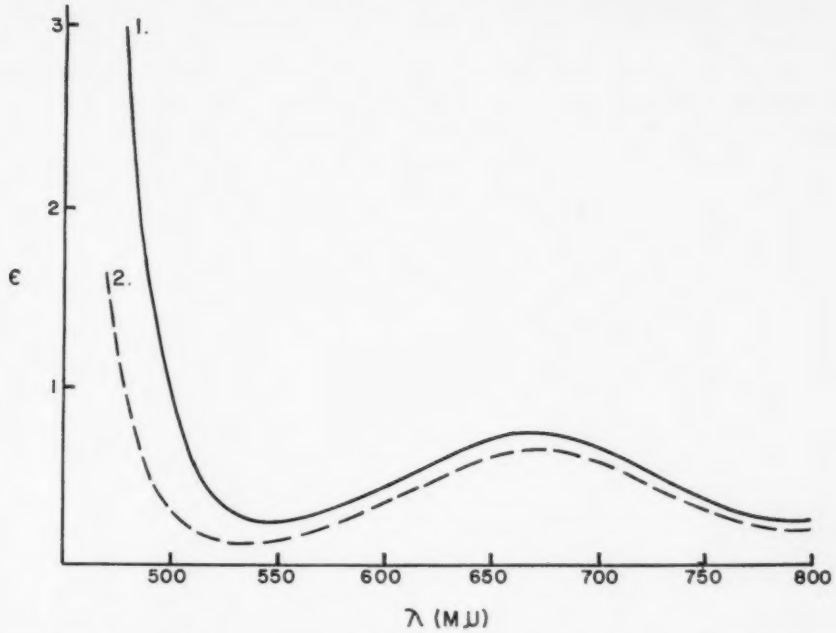


FIG. 5.—Visible absorption spectra of $Fe(C_2O_4)_3^{3-}$. Curve 1, extracted species in $H_2SO_4$-pretreated tri-*n*-hexyl amine in $CHCl_3$; Curve 2, aqueous solution.

TABLE 2.—PER CENT EXTRACTION OF $M(C_2O_4)_2^{2-}$ BY PRIMENE 81-R[a]

| $M(C_2O_4)_2^{2-}$[b] | Free base | Pretreating acids[c] | | | | | |
|---|---|---|---|---|---|---|---|
| | | $H_2SO_4$ | $HNO_3$ | $HClO_4$ | HCl | $HC_2H_3O_2$ | $H_2C_2O_4$ |
| Co(II) | 0·0 | 75·1 | 40·8 | 46·2[d] | 44·4 | 55·9[d] | 48·3[d] |
| Ni(II) | 0·0 | 72·6 | 34·3 | 37·9 | 37·1 | 41·5 | 42·3 |

[a] Primene 81-R concentration was 0·2 M in $CHCl_3$.
[b] The concentration of $M(C_2O_4)_2^{2-}$ was 0·025 M.
[c] 3N acid was used to pretreat the amine $CHCl_3$ solution (a saturated solution of $H_2C_2O_4$ was used).
[d] Concentration of $Co(C_2O_4)_3^{3-}$ was 0·011 M.

that the metallic anion involved in the extraction process is that of the dioxalato metal complex.

## CONCLUSIONS

This study indicates that for the oxalate complex anions studied, their extraction behaviour resembles that of the complex Fe(III) and Co(II) chlorides previously studied[1,2] except that they are less readily extracted than are the smaller tetrahedral $FeCl_4^-$ and $CoCl_4^{2-}$. This difference in extractability could be caused by the larger size and larger charge on the oxalate complexes. These steric considerations could also account for the reversal in the order of extraction efficiency with the type of amine. For the chloride anions, the tertiary amines proved to be the best extractants,

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whereas for the oxalato complexes of this study, the primary amines are better extractants.

The poor extraction of the dioxalato complexes is probably due at least indirectly to the instability of these complexes. Since the complexes must be maintained in solutions containing excess oxalate ion, the competition between oxalate ion and the complex ion could certainly reduce the extraction of the complex.

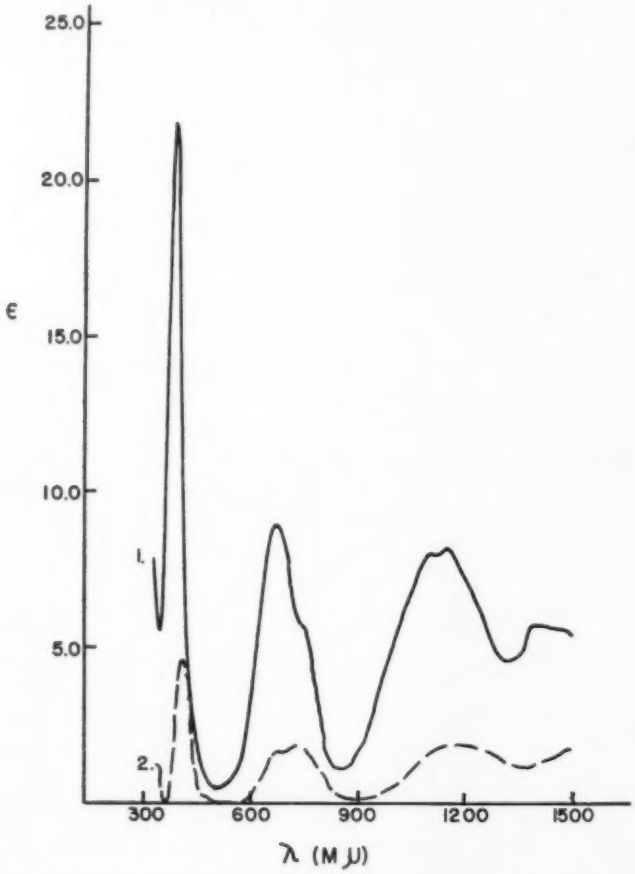


FIG. 6.—Absorption spectra of Ni(II) solutions. Curve 1, $Ni(C_2O_4)_2^{2-}$ in saturated $K_2C_2O_4$ solution; Curve 2, $Ni^{2+}$ in aqueous solution.

It is interesting to note that the difference in the extraction behaviour of the Fe(III) and the Co(III) oxalato complexes is not great although they have entirely different electronic structures. For example the Co(III) complex is thought to be of the "inner orbital" type while the Fe(III) complex is of the "outer orbital" type.[3] The slightly increased extraction of the Fe(III) complex with respect to the Co(III) complex might be due to the greater ionic character of the Fe(III) compound. This is not unreasonable since the extraction mechanism proposed here necessitates the formation of an ion pair composed of the amine radical and the complex anion. This ion pair could perhaps be more easily formed by the more labile Fe(III) complex. To substantiate

this supposition more fully it would be necessary to investigate other similar pairs of anions under similar conditions. We hope to pursue this question further with some extraction studies on other complex anions shortly.

*Acknowledgements*—We would like to thank Mr. F. HOLLAND, Mr. G. MAUS and Mr. F. JUGE for their assistance with some of the experimental work.

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# STUDIES ON MONO- AND DI-*n*-BUTYLPHOSPHORIC ACIDS—IV

## THE EXTRACTION OF URANIUM (VI) FROM AQUEOUS NITRATE SOLUTION BY DI-*n*-BUTYLPHOSPHORIC ACID

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(*Received* 12 *April* 1961)

**Abstract**—The distribution of uranium (VI) between solutions of di-*n*-butylphosphoric acid (HDBP) in various organic diluents and solutions of nitric acid has been studied as a function of the concentrations of HDBP, nitric acid, nitrate ion, and hydrogen ion, and of the nature of the diluent. The distribution coefficient ($D_U$, organic/aqueous) for uranium, which depends markedly on the nature of the diluent and increases in the order

$$CHCl_3 < \text{benzene} < \text{toluene} < CCl_4 < \text{kerosene},$$

can be correlated with the dimerisation constant for HDBP in the diluent. $D_U$ shows a complex dependence on the aqueous nitric acid concentration ($C_{HNO_3}$), being proportional to $C^2_{HNO_3}$ from 0·1–1 M $HNO_3$ and at >8 M $HNO_3$, and to $C_{HNO_3}$ from 3–6 M $HNO_3$. $D_U$ is independent of the aqueous nitrate ion concentration in mixtures of nitric and perchloric acids at a constant ionic strength of one. The implications of these relationships on the mechanism of extraction and the types of complexes formed are discussed, and the extraction of uranium (VI) compared with the extraction of other metals from similar systems.

DETAILED studies have recently been made of the extraction of uranium (VI) from acid perchlorate solution by di-2-ethylhexyl-phosphoric acid (HDEHP) in *n*-hexane[1] and by di-*n*-butyl-phosphoric acid (HDBP) in chloroform and methyl*iso*butylketone (hexone).[2] The principal extraction reaction at low uranium concentration has been interpreted as

$$UO^{2+}_{2(aq)} + 2(HX)_{2(org)} \rightleftharpoons UO_2X_2(HX)_{2(org)} + 2H^+_{(aq)}$$

in which X represents the anion $(RO)_2PO_2^-$. In addition to the $UO_2X_2(HX)_2$ complex, DYRSSEN[2] has postulated a uranyl complex $UO_2X_2$ with only two molecules of HDBP in the hexane system at low concentrations of HDBP and has calculated an equilibrium constant of $10^{4\cdot78}$ for the reaction

$$UO_2X_2 + 2HX \rightleftharpoons UO_2X_2(HX)_2$$

in the hexone phase. With increasing uranium concentration in the organic phase the ratio $[U]_{org}/[HX]_{org}$ approaches 0·5 and indicates the composition $(UO_2)_2X_{2n}$ for the extractable complex, and BAES and co-workers[1] have interpreted their isopiestic and viscosity results in terms of chain polymers of the type $HX_2UO_2X_2UO_2$—$X_2UO_2X_2H$.

[1] C. F. BAES, R. A. ZINGARO and C. F. COLEMAN, *J. Phys. Chem.* **62**, 129 (1958).
[2] D. DYRSSEN and F. KRASOVEC, *Acta Chem. Scand.*, **13**, 561–570 (1959).

The extraction of uranium (VI) from nitric acid solution by dialkylphosphoric acids in various diluents has also been studied[3,4] but no altogether satisfactory interpretation of the data has yet been given. STEWART and HICKS[3] reported the dependence of the distribution coefficient for uranium (VI) ($D_U$, organic/aqueous) on the second or higher power of the dialkylphosphoric acid in dibutyl ether and *n*-hexane as diluents. BROWN and co-workers[4] showed that for the HDBP–benzene–$HNO_3$ system, $D_U$ varied inversely with $C_{HNO_3}$ at $<1$ M $HNO_3$ and directly with $C_{HNO_3}$ at $>3$ M $HNO_3$. They interpreted their results for $>3$M $HNO_3$ by postulating the competing reaction

$$UO_2^{2+} + 2NO_3^- + (HDBP)_2 \rightleftharpoons UO_2(NO_3)_2(HDBP)_2$$

(comparable to the extraction of uranium (VI) by tri-*n*-butyl phosphate (TBP)).

In this paper a more detailed study is reported of the extraction of uranium (VI) from nitrate solution by HDBP in various diluents as a function of the concentrations of HDBP, nitric acid, nitrate ion, hydrogen ion, and the nature of the diluent. The implications of the results on the composition of the complexes formed and on the mechanism of extraction are discussed.

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## EXPERIMENTAL

*Preparation of solutions containing* $^{233}U$

$^{233}U$ was obtained as a solution of uranyl nitrate (4·5 mg/ml) in 0·1 N $HNO_3$. α-pulse analysis showed the α-activity to be due to 99·7% $^{233}U$ and 0·3 per cent to its daughters. The purity was therefore considered to be sufficient for the measurement of distribution coefficients in the range 0·1–20 to better than 5 per cent. An aliquot of 0·005 ml of the above solution of $^{233}U$ was added to 2 ml of the appropriate aqueous solution for each distribution experiment. Nitric acid solutions were made up from A.R. nitric acid and distilled water from a mixed-bed ion-exchange column.

*Source and purity of* HDBP *and diluents*

HDBP was obtained from Albright and Wilson Ltd., Oldbury, and was shown to be >99 per cent pure by electrometric titration and paper chromatography.[5]

$CCl_4$ and toluene were A.R. grade materials and $CHCl_3$ was washed three times with twice its volume of water to remove 1 per cent alcohol. Odourless kerosene, $D_{20}^{20} = 0{\cdot}778$, (Shell Mex and B.P. Ltd., Sunlight House, Quay Street, Manchester; M.O.S. Specification), was used without purification. It had been reported[6] to contain 1% v/v aromatic compounds, 0·5% w/v unsaturated compounds, 0·003% w/v sulphur, and to give a hydrogen: carbon ratio of 2·07.

*Determination of distribution coefficients for uranium*

The α-activity of $^{233}U$ in the organic and aqueous phases was determined in a standard Simpson $2\pi$ proportional counter at 50 per cent geometry; 0·1 ml aliquots of the phases were mounted on 1 in. diameter stainless steel disks and evaporated to dryness under an infra-red lamp. From preliminary experiments it was shown that distribution equilibrium between the phases was achieved in approximately 5 min. All equilibrations were therefore carried out by stirring equal volumes (except where otherwise stated) of the two phases for 10 min at room temperature (20°C) in glass centrifuge tubes, the phases then being separated by centrifugation.

The distribution coefficient for uranium ($D_U$) is defined by:

α-activity in counts/min in organic phase ÷ α-activity in counts/min. in equal volume of aqueous phase.

[3] D. C. STEWART and T. E. HICKS, Report UCRL–861 (1950).
[4] P. G. M. BROWN, J. M. FLETCHER, C. J. HARDY, J. KENNEDY, D. SCARGILL, A. G. WAIN and J. L. WOODHEAD, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, Paper 31; Volume 17, p. 118, United Nations, New York (1959).
[5] C. J. HARDY and D. SCARGILL, AERE C/R 2829 (1959); *J. Inorg. Nucl. Chem.* **10**, 323–7 (1959).
[6] C. J. HARDY and D. SCARGILL, AERE C/R 2830 (1959); *J. Inorg. Nucl. Chem.* **11**, 128–143 (1959).

In the experiments in which lithium nitrate was added to the aqueous phase to maintain constant ionic strength, the deposit of lithium nitrate obtained on the tray after evaporation of a 0·1 ml aliquot of solution prevented accurate determination of the α-activity, due to self-absorption. In these experiments the α-activity in the aqueous phase was therefore measured by

(i) extracting the uranium from 1 ml of the equilibrium aqueous phase into 1 ml of 0·5 M HDBP in toluene by stirring the phases together for 10 mins. (under these conditions $D_U$ was calculated to be

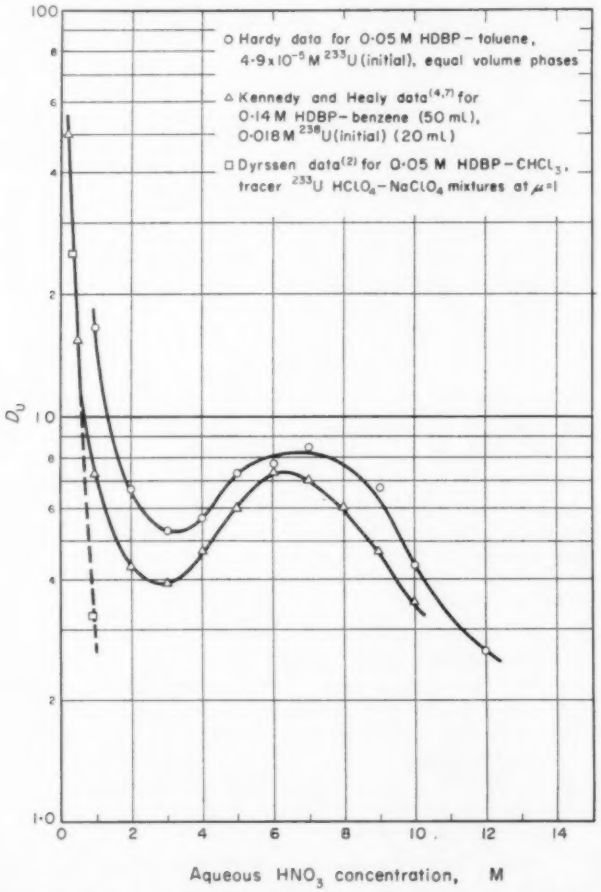


FIG. 1.—The variation of $D_U$ with [$HNO_3$] for HDBP–diluent systems.

~250 at 2 M [$H^+$] and $>5 \times 10^4$ at 0·1 M [$H^+$] and the uranium was quantitatively extracted into the organic phase), and

(ii) counting 0·1 ml of the above organic phase evaporated to dryness on a stainless steel disk (which gives an effectively "weightless" source).

## RESULTS

### *The variation of $D_U$ with the concentrations of* $HNO_3$, $H^+$ *and* $NO_3^-$

The variation of $D_U$ with [$HNO_3$] from 1 to 12 M has been measured for tracer U(VI) and 0·05M HDBP in toluene, and the results are compared in Fig. 1 with results

(i) by KENNEDY[4,7] for 0·018 M U(VI) initially in 0·1–10 M $HNO_3$ and 0·14 M HDBP in benzene (ratio of phase volumes, organic/aqueous = 0·4), and

(ii) By DYRSSEN[2] for tracer U(VI) between 0·05 M HDBP in $CHCl_3$ and $HClO_4$–$NaClO_4$ mixtures at 0·3 and 0·9 M $[H^+]$.

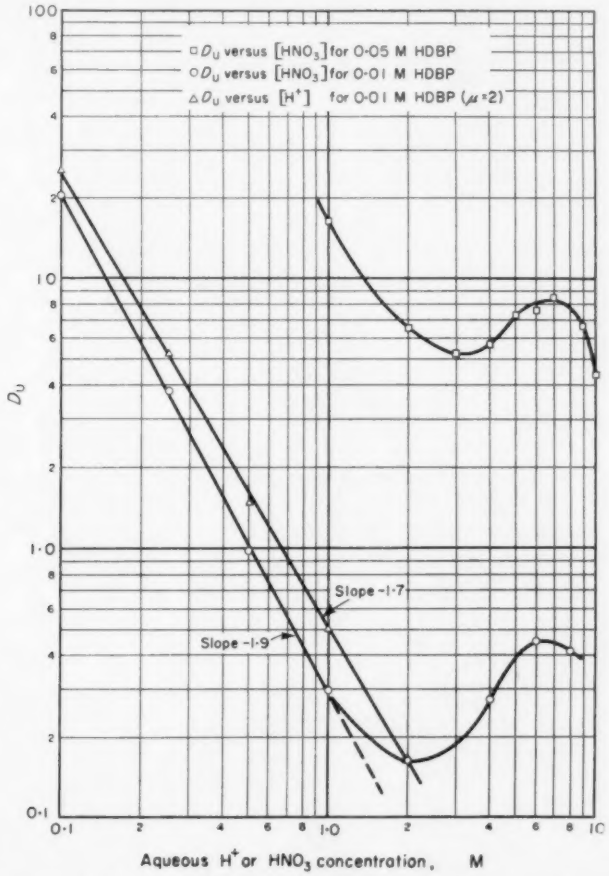
□ $D_U$ versus $[HNO_3]$ for 0·05 M HDBP
○ $D_U$ versus $[HNO_3]$ for 0·01 M HDBP
△ $D_U$ versus $[H^+]$ for 0·01 M HDBP ($\mu$=2)
Slope -1·7
Slope -1·9
$D_U$
Aqueous $H^+$ or $HNO_3$ concentration, M

FIG. 2.—The variation of $D_U$ with $[H^+]$ and $[HNO_3]$ for 0·01 M and 0·05M HDBP–toluene.

The variation of log $D_U$ (for 0·01 M and 0·05 M HDBP–toluene) with log $[HNO_3]$ from 0·1 to 2 M at varying ionic strength, and with log $[H^+]$ at a constant ionic strength of $\mu = 2$ and approximately constant $[NO_3^-] = 2$ M in $HNO_3$–$LiNO_3$ solutions is shown in Fig. 2. The slopes of the straight lines at $<1$ M $[H^+]$ are $-1·9$ and $-1·7$ for varying $\mu$ and constant $\mu$ respectively.

$D_U$ (for 0·01 M HDBP–toluene) is independent of $[NO_3^-]$ at approximately constant $[H^+]$ and constant $\mu = 1$ in $HNO_3$–$HClO_4$ mixtures as shown below:

| $[HNO_3]$(M) | 0 | 0·1 | 1 |
|---|---|---|---|
| $[HClO_4]$(M) | 1 | 0·9 | 0 |
| $D_U$ | 0·35 | 0·33 | 0·33 |

[7] T. V. HEALY and J. KENNEDY, *J. Inorg. Nucl. Chem.* **10**, 128 (1959).

*The variation of $D_U$ with the concentration of* HDBP

The variation of $D_U$ with [HDBP] from $5 \times 10^{-3}$ M to 0·1 M for aqueous phases of 1 and 6 M $HNO_3$ is illustrated in Fig. 3. Approximately straight line log–log plots are obtained with slopes of 2·4 and 1·75 at 1 and 6 M $HNO_3$ respectively. Results

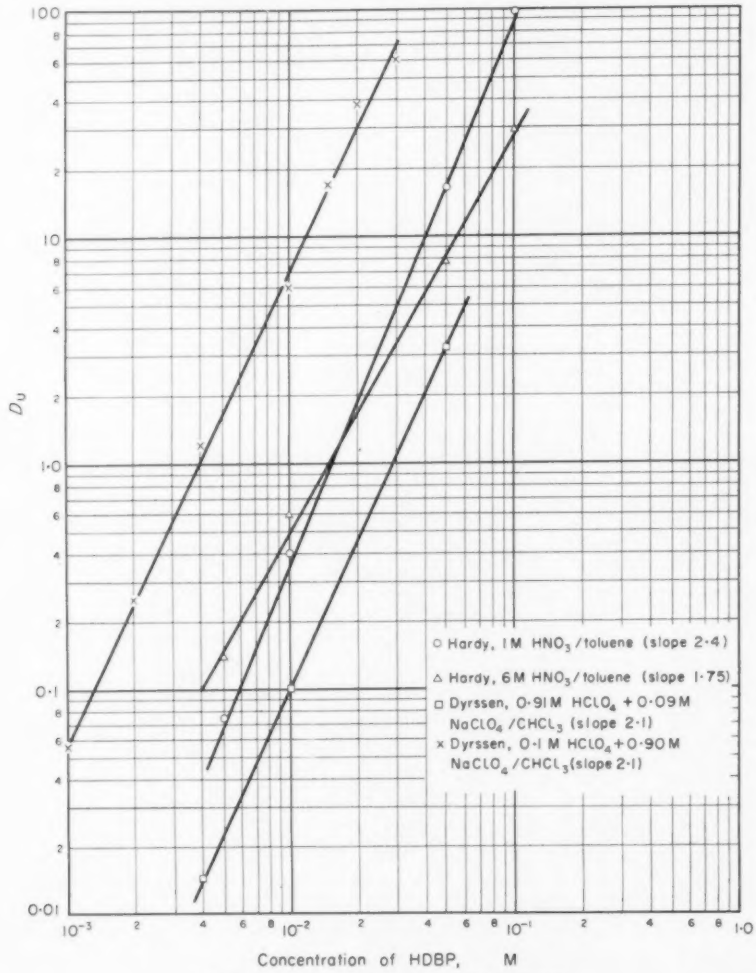


FIG. 3.—The variation of $D_U$ with [HDBP].

by DYRSSEN[2] for 0·1 M $HClO_4$–0·9 M $NaClO_4$ and 0·91 M $HClO_4$–0·09 M $NaClO_4$ and HDBP in $CHCl_3$ are also given in Fig. 3 to show the similarity between perchlorate solutions and nitrate solutions at low [$HNO_3$]. Slopes of 2·1 are obtained from DYRSSEN's results.

*The variation of* $D_U$ *with the diluent*

Values of $D_U$ were measured for 0·05 M HDBP in various diluents and an aqueous phase of 1 M $HNO_3$. Log $D_U$ is plotted in Fig. 4 against the log of the dimerisation

constant ($K_2$) for HDBP in the diluents kerosene, $CCl_4$, $CHCl_3$ and benzene[6], and in toluene.[8]

## DISCUSSION

### *General treatment of the extraction of* U(VI) *from aqueous solution by di-alkylphosphoric acids*

*Acid perchlorate solutions.* The extraction of U(VI) from acid perchlorate solutions by di-alkylphosphoric acids (HX) can be adequately described by the two

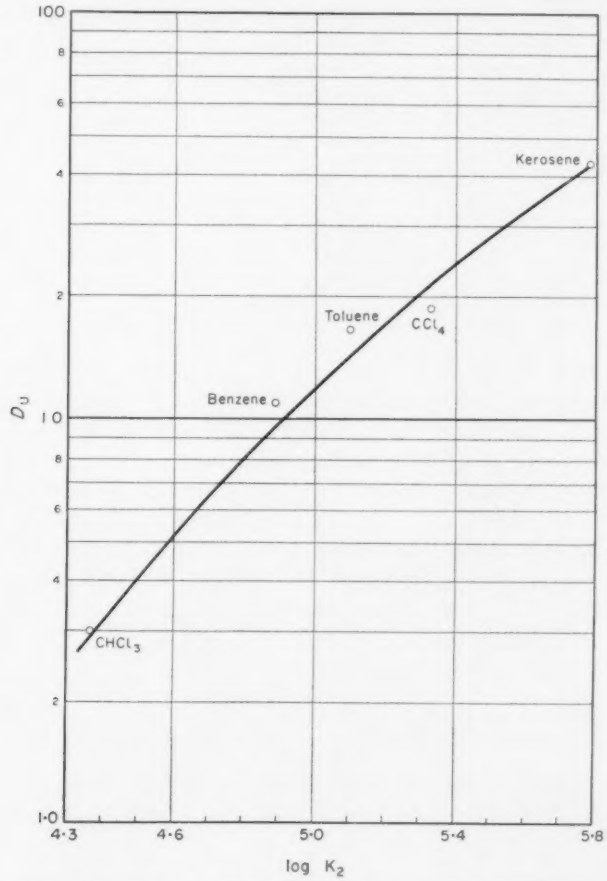


FIG. 4.—Correlation of $D_U$ and log $K_2$ (dimerization constant) for HDBP in various diluents.

principal reactions (1) and (2) for low concentrations of uranium and an excess of HX.

$$UO^{2+}_{2(aq)} + (HX)_{2(org)} \rightleftharpoons UO_2X_{2(org)} + 2H^+_{(aq)} \quad (1)$$

$$UO_2X_{2(org)} + (HX)_{2(org)} \rightleftharpoons UO_2X_2(HX)_{2(org)} \quad (2)$$

The predominant complex in the organic phase at low [U] for [HX] $> \sim 10^{-2}$ M in diluents such as benzene, toluene, $CCl_4$ and $CHCl_3$ is $UO_2X_2(HX)_2$. In diluents

[8] C. J. HARDY and B. F. GREENFIELD. Unpublished work (1959).



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such as hexone, in which hydrogen-bonding can occur between HX and the diluent so that $(HX)_2$ is no longer the predominant HX species, the complex $UO_2X_2$ (probably with added molecules of diluent S to give $UO_2X_2.S_2$) occurs to an appreciable extent. The $UO_2X_2$ species is probably present in an appreciable amount at very low [HX] ($< \sim 10^{-4}$ M) even with the diluents (benzene, hexane, etc.) in which HX has a very high dimerisation constant, since the HX monomer then becomes the predominant species in the organic phase.

*Nitrate solutions.* In nitric acid and nitric acid–metal nitrate solutions a number of additional equilibria must be taken into account to explain the observed variation (e.g. see Fig. 1) of $D_U$ with $[HNO_3]$, $[H^+]$ and $[NO_3^-]$.
These are:

(i) the complexing of $UO_2^{2+}$ by the nitrate ion, represented by the following equilibria

$$UO_2^{2+} + NO_3^- \rightleftharpoons UO_2NO_3^+ \tag{3}$$

$$UO_2NO_3^+ + NO_3^- \rightleftharpoons UO_2(NO_3)_2 \tag{4}$$

(ii) the extraction of $UO_2(NO_3)_2$ by HX by a mechanism analogous to the formation of trialkylphosphate complexes (e.g. TBP).

$$UO_2^{2+} + 2NO_3^- + (HX)_2 \rightleftharpoons UO_2(NO_3)_2 \cdot 2HX \tag{5}$$

(iii) an equilibrium between HX and $HNO_3$ which becomes significant for HDBP in toluene or kerosene at $[HNO_3] >$ about 7 M. This equilibrium reduces the concentration of free HX or $(HX)_2$ and therefore leads to lower values of $D_U$ than would otherwise be obtained. This equilibrium was first reported by HARDY[4] and has been studied recently[8] in more detail for HDBP–toluene and –kerosene solutions.

A quantitative treatment of the extraction of U(VI) from 1–12 M $HNO_3$ by 0·05 M HDBP–toluene was developed previously[9] based upon the above equilibria and experimental results for the appropriate constants. However, the equilibrium between HDBP and $HNO_3$ was not considered to be significant at $<7$ M $HNO_3$, whereas more recent work[10] has shown that it is significant.

Values of $D_U$ calculated from the equation[9]

$$D_U = \frac{[(HDBP)_2]_0 \{(3{\cdot}6 \times 10^4[(HDBP)_2]_0/[H^+]_a^2) + 46[NO_3^-]_a\}}{1 + 0{\cdot}2[NO_3^-]_a + 0{\cdot}05[NO_3^-]_a^2} \tag{6}$$

are compared with the experimental values in Fig. 5. In equation (6) $[(HDBP)_2]_0$ is the concentration of free dimer, i.e. uncomplexed by $HNO_3$, calculated from the equation

$$\text{free } [(HDBP)_2]_0 = \frac{C_A}{2} \cdot \frac{D}{1 + D} \cdot \frac{1}{(1 + 0{\cdot}2C_{u,a})} \tag{7}$$

in which $C_A$ is the initial concentration of HDBP in the organic phase, $D$ is the experimental[10] distribution coefficient of HDBP between the organic and aqueous phases, and $C_{u,a}$ is the concentration of unionised $HNO_3$ in the aqueous phase.[11]

The agreement between the experimental and calculated values of $D_U$ is good up to about 4 M $HNO_3$, but between 4 and 10 M $HNO_3$ the calculated values are too

[9] C. J. HARDY, AERE R 3267 (1960).
[10] C. J. HARDY and B. F. GREENFIELD, Part V. *J. Inorg. Nucl. Chem.* In press **21**, (1961).
[11] E. HESFORD and H. A. C. MCKAY, *Trans. Faraday Soc.* **54**, 573–586 (1958).

low, and above 10 M $HNO_3$ too high. A number of factors may cause this lack of agreement:

(i) the values of $K_{UO_2NO_3^+} = 0{\cdot}2$ and $K_{UO_2(NO_3)_2} = 0{\cdot}25$ for the equilibria in equations (3) and (4) respectively, probably do not hold for solutions of ionic strength different to that ($\mu = 7$) in which they were measured[11] or deduced (in general, formation

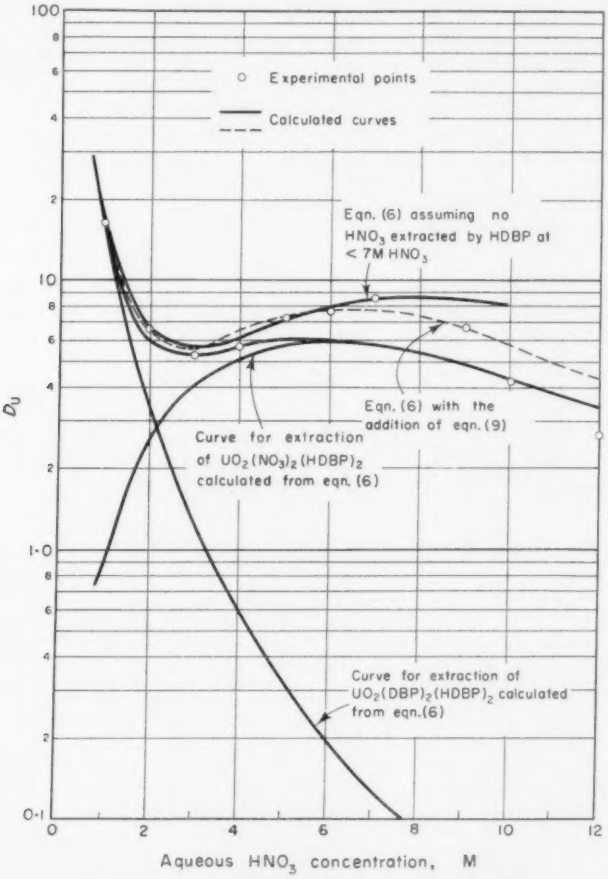
Experimental points
Calculated curves
Eqn. (6) assuming no HNO3 extracted by HDBP at < 7M HNO3
Eqn. (6) with the addition of eqn. (9)
Curve for extraction of UO2(NO3)2(HDBP)2 calculated from eqn. (6)
Curve for extraction of UO2(DBP)2(HDBP)2 calculated from eqn.(6)
DU
Aqueous HNO3 concentration, M

FIG. 5.—Calculated and experimental values of $D_U$ for the 0·05 M HDBP-toluene–$HNO_3$ system.

constants of this type decrease with increasing ionic strength and this effect has not been taken into account due to lack of information). A reduction of $K_{UO_2(NO_3)_2}$ to 0·15 leads to an increase of about 15 per cent in $D_U$ in the range of 5–10 M $HNO_3$, compared to about 5 per cent at 2 M $HNO_3$.

(ii) the presence of other complexes between uranium and HDBP in the organic phase, e.g. $UO_2NO_3 \cdot DBP(HDBP)_2$ or $H[UO_2(NO_3)_3](HDBP)_2$, of which the former seems more probable as a link between $UO_2(DBP)_2(HDBP)_2$ and $UO_2(NO_3)_2(HDBP)_2$. However, the contribution to the overall $D_U$ of this complex calculated with the equation

$$D_U = \frac{K[NO_3^-]_a[(HDBP)_2]_0^{3/2}}{[H^+]_a(1 + 0{\cdot}2[NO_3^-]_a + 0{\cdot}05[NO_3^-]_a^2)} \quad (8)$$

TABLE 1.—COMPARISON OF $D_M$ FOR VARIOUS METALS

| Metal | 0·5 M HDBP/diluent/0·1 M $HNO_3$ | | | 0·5 M HDEHP/diluent/0·1 M $HNO_3$ | | | 0·5 M HDEHP/diluent/10 M $HNO_3$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $D_M$ | Diluent | Reference | $D_M$ | Diluent | Reference | $D_M$ | Diluent | Reference |
| $Zr^{4+}$ | $\sim 6 \times 10^7$ | Toluene | 12 | — | — | — | $\sim 2 \times 10^7$ | Toluene | 12 |
| $Y^{3+}$ | $1{\cdot}7 \times 10^4$ | $CHCl_3$ | 13 | — | — | — | $\sim 1$ | $CHCl_3$ | 13 |
| $UO_2^{2+}$ | $\sim 4 \times 10^5$ | Toluene | This work | — | — | — | $\sim 1 \times 10^3$ | Toluene | This work |
| | $1{\cdot}2 \times 10^3$ | $CHCl_3$ | 2 | — | — | — | — | — | — |
| | $4{\cdot}5 \times 10^2$ | Hexone | 2 | — | — | — | — | — | — |
| $Be^{2+}$ | $\sim 200$ | Toluene | 8 | $\sim 100$ | Toluene | 8 | 0·15 | Toluene | 8 |
| $La^{3+}$ | — | — | — | 0·22 | Hexane (0·1 M HCl) | 14 | $\sim 1{\cdot}5 \times 10^{-3}$ | Heptane | 16 |
| $Ba^{2+}$ | — | — | — | $\sim 1 \times 10^{-3}$ | Hexane (0·1 M HCl) | 14 | — | — | — |
| $Sr^{2+}$ | $1{\cdot}5 \times 10^{-3}$ | $CHCl_3$ | 13 | $1{\cdot}8 \times 10^{-3}$ | Hexane (0·1 M HCl) | 14 | — | — | — |
| $Co^{2+}$ | $< 10^{-4}$ | Toluene | 8 | — | — | — | — | — | — |
| $Ce^{4+}$ | — | — | — | — | — | — | $\sim 3 \times 10^4$ | Heptane | 16 |
| $Bk^{4+}$ | — | — | — | — | — | — | $\sim 2 \times 10^5$ | Heptane | 16 |

would decrease uniformly as $[HNO_3]_a$ increases and would not lead to any better agreement between the experimental and calculated values of $D_U$. The contribution of a trinitrato complex calculated with the equation

$$D_U = \frac{K[NO_3^-]_a^3[H^+]_a[(HDBP)]_0}{(1 + 0{\cdot}2[NO_3^-]_a + 0{\cdot}05[NO_3^-]_a^2)} \quad (9)$$

increases sharply with $[HNO_3]_a$ to a maximum between 7 and 8 M $HNO_3$ and then decreases sharply; equation (6) and equation (9) (using a value of $K = 0{\cdot}66$) give a better fit than equation (6) alone (see dotted curve in Fig. 5).

(iii) the free dimer concentrations calculated for 0·05 M HDBP in toluene from the equation deduced[10] for 0·5 M HDBP in toluene may be too low; if it is assumed that a negligible amount of $HNO_3$ is extracted by 0·05 M HDBP at $<7$ M $HNO_{3,aq}$ equation (15) gives very good agreement with the experimental points up to 7 M $HNO_3$ (see Fig. 5 and reference (10)).

*Comparison of the extraction of* U(VI) *with the extraction of other metals from aqueous solution by dialkylphosphoric acids.* A detailed study of the extraction by dialkylphosphoric acids of metals other than U(VI) has only been made for Zr(IV) with HDBP,[12] Y(III) with HDBP,[13] and Pa(V) with di-*iso*-amylphosphoric acid.[14,15] Distribution coefficients for various other metals e.g. Sr, Ba, Y, La, Ce(IV), Ce(III), Bk(IV), Bk(III), have been reported[16] in HDEHP–dilute HCl and –10 M $HNO_3$ systems, and for U(IV), V(IV), Al, Mo, Fe(III), Ti and Th in HDEHP–dilute HCl and –dilute $H_2SO_4$ systems.[17]

Although intercomparison of the systems is difficult, the values of $D_M$ in the various systems have, wherever possible, been converted to the values to be expected in the three systems.

(i) 0·5 M HDBP/diluent/0·1 M $HNO_3$,

(ii) 0·5 M HDEHP/diluent/0·1 M $HNO_3$, and

(iii) 0·5 M HDEHP/diluent/10 M $HNO_3$,

by interpolation between, or extrapolation of, the experimental values, assuming that

$$D_M \propto [\text{free dimer}]_{org}^n [H^+]_{aq}^{-n}$$

where $n$ is the charge on the cation. Values of $D_M$ are compared in Table 1, from which the following order of extraction is obtained for the extraction of metals from dilute acid solution:

$$Zr(IV) > Y(III) > U(VI) > Be(II) > La(III) > Sr(II),\ Ba(II) > Co(II).$$

The order for metals in 10 M $HNO_3$ solution, from which extraction occurs by the two different mechanisms of "chelation" and "solvation" to varying extents for the different metals is:

$$Zr(IV) > Bk(IV) > Ce(IV) > U(VI) > Y(III) > Be(II) > Bk(III) > Ce(III) > La(III).$$

[12] C. J. Hardy and D. Scargill, AERE R 2945 (1959). Part III. *J. Inorg. Nucl. Chem.* **17,** 337 (1961).
[13] D. Dyrssen, *Acta Chem. Scand.* **11,** 1277 (1957).
[14] V. B. Shevchenko, V. A. Mikhailov and Yu. P. Zaval'skii, *Zh. Neorg. Khim.* **3,** 1955–1958 (1958).
[15] V. A. Mikhailov, V. B. Shevchenko and V. A. Kolganov, *Zh. Neorg. Khim.* **3,** 1959–1964 (1958).
[16] D. F. Peppard, G. W. Mason and S. W. Moline, *J. Inorg. Nucl. Chem.* **5,** 141–6 (1957).
[17] C. A. Blake, D. E. Horner and J. M. Schmitt, Report ORNL–2259 (1959).

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Values of the equilibrium constant ($K_1$) for the reaction

$$M^{n+}_{(aq)} + n(HX)_{2(org)} \rightleftharpoons M(X.HX)_{n(org)} + nH^{+}_{(aq)}$$

$$\text{defined by } K_1 = \frac{[M(X.HX)_n]_{org}[H^+]^n_{aq}}{[M^{n+}]_{aq}[(HX)_2]^n_{org}} = \frac{D_M.[H^+]^n_{aq}}{[(HX)_2]^n_{org}}$$

have been calculated for a few of the above systems (Table 2). The values of $K_1$ are corrected for (i) the complexing of the metal ion by the anion in the aqueous

TABLE 2.—VALUES OF $K_1$ FOR VARIOUS METALS

| Metal | Aqueous phase | Organic phase | $K_1$ | Reference |
|---|---|---|---|---|
| U (VI) | $HNO_3$ and nitrate | HDBP–toluene | $3{\cdot}6 \times 10^4$ | This work |
| U (VI) | Perchlorate | HDBP–$CHCl_3$ | $3{\cdot}8 \times 10^3$ | 2 |
| | | HDBP–hexone | $3{\cdot}16 \times 10^4$ | 2 |
| U (VI) | Perchlorate | HDEHP–hexane | $4{\cdot}0 \times 10^4$ | 1 |
| U (VI) | HCl | HDEHP–kerosene | $3{\cdot}4 \times 10^4$ | 17 |
| $Y^{3+}$ | $HNO_3$ | HDBP–$CHCl_3$ | $1{\cdot}4 \times 10^3$ | 13 |
| $Y^{3+}$ | HCl | HDEHP–hexane | $5 \times 10^2$ | 16 |
| $La^{3+}$ | HCl | HDEHP–hexane | $3 \times 10^{-3}$ | 16 |
| $Be^{2+}$ | $HNO_3$ | HDBP–toluene | 35 | 8 |
| | | HDEHP–toluene | 19 | 8 |

phase, e.g. U(VI) with $NO_3^-$, $Cl^-$ or $SO_4^{2-}$, using published formation constants,[18] and (ii) the amount of X and HX present in the metal complex.

The values of $K_1$ for U(VI) with HDBP and HDEHP in toluene, hexane, and kerosene are approximately the same ($3{\cdot}7 \pm 0{\cdot}3 \times 10^4$) from the various published work. The few available values for different metals are in the order

$$U(VI) > Y(III) > Be(II) > La(III),$$

which agrees with the order of extraction of these metals from strong $HNO_3$ and not from dilute acid.

[18] *Stability Constants, Part II, Inorganic Ligands*, The Chemical Society, London (1958).

J. Inorg. Nucl. Chem., 1961, Vol. 21, pp. 359 to 365. Pergamon Press Ltd. Printed in Northern Ireland

# STUDIES ON MONO- AND DI-*n*-BUTYLPHOSPHORIC ACIDS—V

## THE EXTRACTION OF NITRIC ACID FROM AQUEOUS SOLUTION BY DI-*n*-BUTYLPHOSPHORIC ACID AND FURTHER RESULTS ON THE DISTRIBUTION OF DI-*n*-BUTYLPHOSPHORIC ACID IN AQUEOUS-ORGANIC SOLVENT SYSTEMS

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**Abstract**—The distribution of $^{32}P$-labelled di-*n*-butylphosphoric acid (HDBP) between toluene and aqueous nitric acid has been measured as a function of (i) the concentration of $HNO_3$ from 0·5–12 M for 0·01, 0·05 and 0·5 M HDBP, and (ii) the concentration of HDBP from $10^{-5}$–0·5 M for 1, 6 and 10 M $HNO_3$. The dimerization constant and monomer distribution coefficient for HDBP in toluene–1 M $HNO_3$ correspond to log $K_2 = 5{\cdot}09$ and log $K_d = -0{\cdot}70$. The amount of $HNO_3$ extracted by a 0·5 M solution of HDBP in toluene can be expressed by the relation $C_{HNO_3(org)} = 0{\cdot}051 C_{HNO_3(unionized,aq)}$ up to 12 M $HNO_3$ in the aqueous phase; approximately 20 per cent of the uncomplexed HDBP and 40 per cent of the HDBP·$HNO_3$ complex are hydrated. A third phase forms in the 0·5 M HDBP–kerosene–$HNO_3$ system at >4 M $HNO_3$ in the aqueous phase; at 12 M $HNO_3$ the third phase has the empirical formula HDBP·$HNO_3$·$H_2O$.

In recent investigations of the extraction of uranium,[1] beryllium[2] and zirconium[3] from aqueous solution by di-*n*-butylphosphoric acid (HDBP) we have measured the distribution coefficient of the metal between the aqueous phase and solutions of HDBP in toluene. We have previously[4] measured the solubility and distribution of HDBP in a number of aqueous–organic solvent systems and have now extended the work to include toluene. We have also examined the extraction of nitric acid from aqueous solution by HDBP in organic solvents, which has only received brief mention before.[5]

## EXPERIMENTAL

### *Purification of materials*

Inactive HDBP was separated from a commercial mixture of "acid butyl phosphates" (from Albright and Wilson Ltd., London) by the solvent extraction techniques previously described.[6] The HDBP was shown by electrometric titration and paper chromatography[6] to contain <0·1 per cent of the mono-*n*-butylphosphoric acid ($H_2MBP$), and to be free from phosphoric acid and non-acidic impurities.

$^{32}P$-labelled HDBP (from the Radiochemical Centre, Amersham, England) was analysed by paper

(1) C. J. HARDY, AERE-R3267 (1960).
(2) C. J. HARDY, B. F. GREENFIELD and D. SCARGILL, *J. Chem. Soc.* 174 (1961).
(3) C. J. HARDY and D. SCARGILL, *J. Inorg. Nucl. Chem.*, **17**, 337 (1961).
(4) C. J. HARDY and D. SCARGILL, *J. Inorg. Nucl. Chem.* **11**, 128 (1959).
(5) P. G. M. BROWN, J. M. FLETCHER, C. J. HARDY, J. KENNEDY, D. SCARGILL, A. G. WAIN and J. L. WOODHEAD, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, Paper 31, Vol. 17, p. 118. United Nations, New York (1959).
(6) C. J. HARDY and D. SCARGILL, *J. Inorg. Nucl. Chem.* **10**, 323 (1959).

chromatography and found to contain 0·5% $H_2MB^{32}P$. The $H_2MB^{32}P$ was removed from a solution of the mixture in toluene by stirring it with an equal volume of 1 M $HNO_3$ and separating the phases by centrifugation. The $HDB^{32}P$ was recovered by evaporating off the toluene under water-pump vacuum, and vacuum drying the product at 0·1 mm Hg and $<50°C$; its purity was 99·95 per cent and specific activity 56 mc/g.

The organic solvents used without further purification were sulphur-free toluene, A.R. benzene, hexane free from aromatic hydrocarbons, and *n*-dodecane (L. Light & Co. Ltd., Colnbrook, Bucks); nitric acid solutions were prepared from A.R. concentrated nitric acid.

*Distribution coefficient measurements*

The net distribution coefficient ($D_{HDBP}$) for HDBP, defined as corrected $\beta$-activity in organic phase/corrected $\beta$-activity in equal volume of aqueous phase, was measured radiometrically with $^{32}P$-labelled HDBP. Equal volumes of each phase were stirred together for 10 min at 25°C (no variation in $D_{HDBP}$ was found for times of stirring from 1–60 min) and the phases were separated by centrifugation. The $\beta$-activity of 10 ml of each phase was measured in a standard liquid counter tube (type M6, 20th Century Electronics). Calibration curves for variation of count-rate with the density of the solution were determined in a similar way to that described by DYRSSEN.[7]

The distribution coefficient for nitric acid between aqueous solutions and solutions of HDBP in organic solvents was measured by titration of the nitric acid in the aqueous phase and after washing the nitric acid from the organic phase into water, or more simply by direct titration of the organic phase. The nitric acid in 0·5 M HDBP solutions in toluene was measured after washing it back into an aqueous phase; in each experiment 5 ml of each phase were stirred together for 10 min, and the phases were separated by centrifugation. 4 ml of the organic phase was then removed and stirred for 5 min with 15 ml water; the phases were separated, and the 15 ml of aqueous nitric acid washed twice with 5 ml of toluene to remove traces of dissolved and entrained HDBP, and finally titrated electrometrically with standard NaOH solution. One of the above results was checked by analysing the nitrate present in the organic phase by the Lunge Nitrometer method.[8] The nitric acid in the organic phase was directly titrated in the experiments with 0·5 and 0·05 M HDBP in kerosene; 25 ml of each phase for 0·5 M HDBP (or 50 ml for 0·05 M HDBP) were stirred together for 10 min, separated by centrifugation, and 20 (or 45) ml of each phase titrated electrometrically with standard NaOH solution.

*Analysis of the third phase in the* HDBP–*kerosene*–$HNO_3$ *system*

An aliquot part of the third phase formed by stirring equal volumes of 12 M $HNO_3$ and 0·5 M HDBP (labelled with $HDB^{32}P$ and of known specific activity) in kerosene for 10 min at 25°C was titrated to determine the total amount of acid present ($HNO_3$ + HDBP). The amount of HDBP present was determined by $\beta$-counting an aliquot part of the third phase diluted to 10 ml with toluene in a liquid counter. The amount of $HNO_3$ was obtained by difference. The water content of the third phase and of other solutions was determined by the standard Karl Fischer method.

## RESULTS AND DISCUSSION

### *Distribution of* HDBP *between aqueous nitric acid and kerosene or toluene*

The dependence of $D_{HDBP}$ on the initial concentration of $HNO_3$ in the aqueous phase for 0·01, 0·05 and 0·5 M HDBP in toluene is shown in Fig. 1. The dependence of $D_{HDBP}$ on the initial HDBP concentration ($C_A$) in toluene for aqueous phases of 1, 6 and 10 M $HNO_3$ is shown in Fig. 2.

The large variation of $D_{HDBP}$ with the composition of the paraffinic hydrocarbon diluent is illustrated by the following results for 0·01 M HDBP and 1 M $HNO_3$:

| Diluent | Kerosene | Hexane | n-Dodecane | Cf. Toluene |
|---|---|---|---|---|
| $D_{HDBP}$ | 0·64 | 1·43 | 2·84 | 8·9 |

[7] D. DYRSSEN, *Acta Chem. Scand.* **11**, 1277 (1957).
[8] A. I. VOGEL, *A Textbook of Quantitative Inorganic Analysis*, p. 808. Longmans, London (1951).

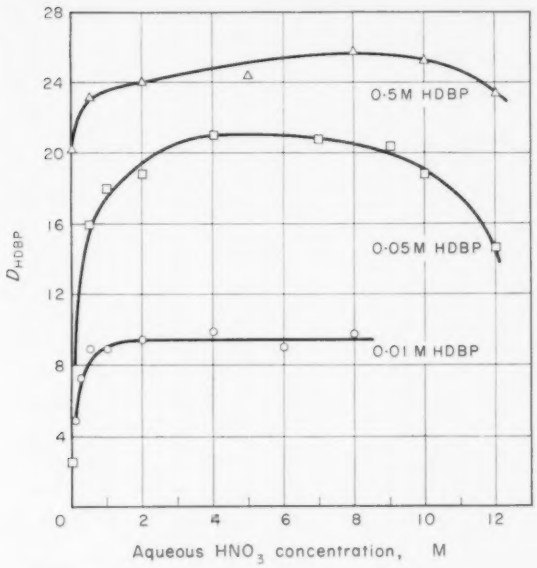


FIG. 1.—Dependence of $D_{HDBP}$ on the aqueous concentration of nitric acid in the HDBP–toluene–nitric acid system.

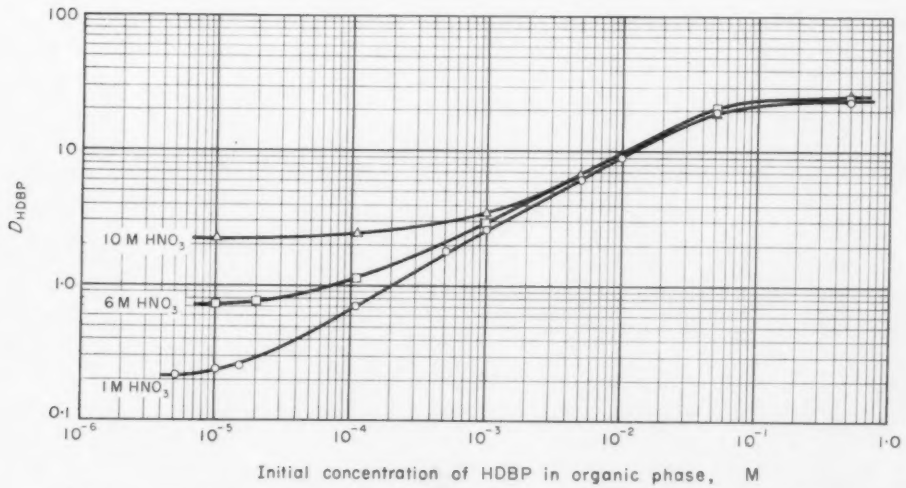


FIG. 2.—Dependence of $D_{HDBP}$ on the initial concentration of HDBP in the organic phase.

The distribution of 0·5 M HDBP between kerosene and aqueous nitric acid gave the results:

| Aqueous phase | Water | 1 M $HNO_3$ | 4–12 M $HNO_3$ |
|---|---|---|---|
| $D_{HDBP}$ | 7·02 | 13·0 | Third phase formed |

The third phase formed with kerosene and 12 M $HNO_3$ had the following composition:

| | |
|---|---|
| Total acidity of third phase | 6·93 M |
| HDBP concentration by $\beta$-counting | 3·42 M |
| $HNO_3$ concentration by difference | 3·51 M |
| $H_2O$ concentration by Karl Fischer method | 3·53 M |
| Density of third phase | 1·10 g/ml |
| Ratio of HDBP:$HNO_3$:$H_2O$ | = 1:1·03:1·03 |

*Calculation of dimerization constant ($K_2$) for* HDBP *in toluene, and distribution coefficient of* HDBP *monomer ($K_d$) and dimer ($K_D$)*

The values of $K_2$, $K_d$ and $K_D$ for HDBP in toluene–1 M $HNO_3$ calculated as described before[6] are compared below with those for benzene and kerosene. The same symbols are used in this work as before except that in accordance with IUPAC $K$ is used instead of $k$ for equilibrium constants.

| Diluent | log $K_2$ | log $K_d$ | log $K_D$ |
|---|---|---|---|
| Toluene | 5·09 | −0·70 | 2·6 |
| | ±0·06 | ±0·02 | ±0·2 |
| Benzene | 4·88 | −0·42 | 2·9 |
| | ±0·06 | ±0·02 | ±0·2 |
| Kerosene | 5·78 | −1·96 | 0·75 |
| | ±0·06 | ±0·02 | ±0·2 |

The experimental errors were estimated from the fit obtained between the normalized curve log $y$ = log $(x + 1)$ and the experimental points in the plot of log $D_{HDBP}$ versus log (concentration of HDBP in aqueous phase).

*Distribution of* $HNO_3$ *between aqueous solutions and solutions of* HDBP *in toluene and kerosene*

The results are summarized in Table 1 for the systems 0·05 M HDBP–kerosene–$HNO_3$ and 0·05 M HDBP–toluene–$HNO_3$ and in Table 2 for 0·5 M HDBP–toluene–$HNO_3$. The concentrations in mole/litre at equilibrium are as follows:

$C_{HNO_3(aq)}$ $HNO_3$ in the aqueous phase,

$C_{HNO_3(org)}$ $HNO_3$ in the organic phase, corrected for the concentration of $HNO_3$ extracted in the absence of HDBP,

$C_{HNO_3(u,aq)}$ unionized $HNO_3$ in the aqueous phase from the data of KRAWETZ, kindly made available by HESFORD and MCKAY[9],

$C_{org}$ total HDBP in the organic phase,

$C_{F(org)}$ "free" HDBP in the organic phase, i.e. that not complexed with $HNO_3$ calculated from $(C_{org} - C_{HNO_3(org)})$ assuming a 1:1 complex.

Since the principal HDBP species in the organic phase is the dimer $(HDBP)_2$, due to the high dimerization constant in toluene, the equilibrium constant ($K_1$) was first calculated for the results in Table 2 using the equation

$$(HDBP)_{2(org)} + HNO_{3(u,aq)} \rightarrow (HDBP)_2 \cdot HNO_{3(org)} \qquad (1)$$

[9] E. HESFORD and H. A. C. MCKAY, *Trans. Faraday Soc.* **54**, 573 (1958).

from $$K_1 = \frac{[(HDBP)_2 \cdot HNO_3]_{org}}{[(HDBP)_2]_{org}[HNO_3]_{u,aq}} = \frac{C_{HNO_3(org)}}{(C_{org} - 2C_{HNO_3(org)})\, C_{HNO_3(u,aq)}}$$

However, $K_1$ (Table 2) shows considerable scatter in the limited range of 2–8 M $HNO_3$ in which it can be calculated. A better fit is obtained by assuming complex formation with the monomer:

$$HDBP_{org} + HNO_{3(u,aq)} \rightarrow HDBP \cdot HNO_{3(org)} \quad (2)$$

TABLE 1.—DISTRIBUTION OF $HNO_3$ IN THE 0·05 M HDBP–KEROSENE–$HNO_3$ AND 0·05 M HDBP–TOLUENE–$HNO_3$ SYSTEMS

| Diluent | $C_{HNO_3\,(aq)}$ | $C_{HNO_3\,(org)}$ | $C_{HNO_3\,(u,aq)}$ | $C_{org}$ | $C_{F(org)}$ | $C_{HNO_3\,(org)}$ No HDBP |
|---|---|---|---|---|---|---|
| Kerosene | 8·99 | 0·011 | 3·87 | 0·0296 | 0·0185 | 0·001 |
| | 9·99 | 0·012 | 4·99 | 0·0273 | 0·0152 | 0·001 |
| | 11·99 | 0·013 | 7·50 | 0·0211 | 0·0081 | 0·002 |
| Toluene | 8·975 | 0·025 | 3·80 | 0·0475 | 0·0225 | 0·033 |
| | 9·97 | 0·031 | 4·96 | 0·0475 | 0·0165 | 0·050 |
| | 11·96 | 0·040 | 7·45 | 0·0465 | 0·0065 | 0·108 |

TABLE 2.—DISTRIBUTION OF $HNO_3$ IN THE 0·5 M HDBP–TOLUENE–$HNO_3$ SYSTEM

| $C_{HNO_3\,(aq)}$ | $C_{HNO_3\,(org)}$ | $C_{HNO_3\,(u,aq)}$ | $C_{org}$ | $C_{F(org)}$ | $C_{HNO_3\,(org)}$ No HDBP | $C_{HNO_3\,(org)}$ Calc. | $K_1$ | $K_1^1$ |
|---|---|---|---|---|---|---|---|---|
| 2·02 | 0·008 | 0·08 | 0·480 | 0·472 | — | 0·004 | 0·4 | 0·2 |
| 4·11 | 0·023 | 0·65 | 0·480 | 0·457 | — | 0·033 | 0·16 | 0·08 |
| 6·07 | 0·082* | 1·50 | 0·481 | 0·399 | 0·006 | 0·077 | 0·35 | 0·14 |
| 7·97 | 0·159 | 2·90 | 0·482 | 0·323 | 0·020 | 0·148 | 0·67 | 0·17 |
| 9·90 | 0·250 | 4·90 | 0·481 | 0·231 | 0·048 | 0·25 | — | 0·22 |
| 11·77 | 0·328 | 7·25 | 0·480 | 0·152 | 0·105 | 0·37 | — | 0·30 |
| 13·43 | 0·52 | 9·6 | 0·477 | — | 0·18 | 0·49 | — | — |
| 14·86 | 0·87 | 11·7 | — | — | 0·36 | 0·60 | — | — |

* Analysis directly on organic phase with Lunge nitrometer gave 0·077 M.

for which the equilibrium constant

$$K_1^1 = \frac{[HDBP \cdot HNO_3]_{org}}{[HDBP]_{org}[HNO_3]_{u,aq}} = \frac{C_{HNO_3(org)}}{C_{F(org)} \cdot C_{HNO_3(u,aq)}} = 0{\cdot}2 \pm 0{\cdot}1$$

from 2 to 12 M $HNO_3$; above 13 M $HNO_3$ the ratio of $HNO_3$ to HDBP in the organic phase is greater than unity and a complex $HDBP \cdot 2HNO_3$ is probably formed.

The results (Table 1) for HDBP in kerosene also give a value of $K_1^1 = 0{\cdot}2$ but the results for 0·05 M HDBP in toluene give values from 0·3 to 0·8 and the poor agreement is probably due to the low accuracy of the values of $C_{HNO_3(org)}$ after correction for the large amount of $HNO_3$ co-extracted by the toluene itself.

A plot of $C_{HNO_3(org)}$ versus $C_{HNO_3(u,aq)}$ gives a straight line of slope 0·051; calculated values of $C_{HNO_3(org)} = 0{\cdot}051 C_{HNO_3(u,aq)}$ are given in Table 2 and are in reasonably good agreement with the experimental values from 6 to 12 M $HNO_3$.

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The *total* amount of $HNO_3$ extracted by a 0·5 M solution of HDBP in toluene can be calculated from the above equations, together with the equation for the extraction of $HNO_3$ by the diluent alone.[10] The equations for toluene are as follows:

$$\begin{aligned} \textit{Total}\ [HNO_3]_{org} &= C_{HNO_3(org)}(HDBP) + C_{HNO_3(org)}(\text{toluene}) \\ &= 0{\cdot}051 C_{HNO_3(u,aq)} + 1{\cdot}2 \times 10^{-3}\ \text{M}\ C_{HNO_3(u,aq)} \\ &\quad + 1{\cdot}7 \times 10^{-3} C^2_{HNO_3(u,aq)} \\ &= 0{\cdot}052 C_{HNO_3(u,aq)} + 1{\cdot}7 \times 10^{-3} C^2_{HNO_3(u,aq)} \end{aligned}$$

*Water content of the* HDBP *phase in contact with* $H_2O$ *and* $HNO_3$

The water and total acid concentrations in the organic phase for a series of HDBP/toluene–$H_2O$ and –$HNO_3$ solutions are given in Table 3, together with the

TABLE 3.—WATER CONTENT OF THE HDBP PHASE

| Organic phase | Aqueous phase (initially equal volume) | Total acid concentration in aq. phase (M) | Total acid concentration in org. phase (M) | Water concn. in org. phase (M) | Mole ratio $H_2O$:HDBP in org. phase |
|---|---|---|---|---|---|
| Toluene | $H_2O$ | — | — | 0·017 | — |
| undiluted HDBP | $H_2O$ | 0·09 | 4·62 | 5·52 | 1·20 |
| 1 M HDBP–toluene | $H_2O$ | 0·034 | 1·025 | 0·23 | 0·20 |
| 0·5 M HDBP–toluene | $H_2O$ | 0·028 | 0·485 | 0·12 | 0·22 |
| 0·5 M HDBP–toluene | 6 M $HNO_3$ | 5·96 | 0·618 | 0·14 | 0·29 |
| 0·5 M HDBP–toluene | 10 M $HNO_3$ | 9·88 | 0·845 | 0·21 | 0·43 |
| 0·5 M HDBP–toluene | 12 M $HNO_3$ | 12·0 | 0·957 | 0·26 | 0·54 |

TABLE 4.—AMOUNTS OF VARIOUS WATER COMPLEXES IN HDBP–TOLUENE–$HNO_3$ PHASES

| Aqueous acid conc., (M) | Total water concn. in org. phase, (M) | Water concn. (M) in org. phase complexed with: | | | | Ratio $\frac{H_2O\ (iii)}{HNO_3\ (iii)}$ |
|---|---|---|---|---|---|---|
| | | (i) Toluene | (ii) HDBP | (iii) HDBP $HNO_3$ | (iv) $HNO_3$ extd by toluene | |
| 0 | 0·12 | 0·017 | 0·10 | — | — | — |
| 6 | 0·14 | 0·017 | 0·073 | 0·047 | 0·003 | 0·36 |
| 10 | 0·21 | 0·017 | 0·035 | 0·132 | 0·024 | 0·41 |
| 12 | 0·26 | 0·017 | 0·023 | 0·17 | 0·055 | 0·46 |

solubility of water in toluene. Undiluted HDBP is complexed with 1·2 $H_2O$ molecules per HDBP molecule, but in solutions of HDBP in toluene only ~20 per cent of the HDBP is complexed with $H_2O$, i.e. 0·2 mole of $H_2O$ per mole of HDBP. The predominant species in HDBP solutions in toluene in contact with water are therefore the unhydrated dimer, $(HDBP)_2$, and either a hydrated monomer $HDBP{\cdot}H_2O$, or a hydrated dimer, $(HDBP)_2{\cdot}H_2O$ [or possibly $(HDBP{\cdot}H_2O)_2$].

[10] C. J. HARDY, B. F. GREENFIELD and D. SCARGILL, *J. Chem. Soc.* 90 (1961).

In solutions of HDBP in toluene in contact with aqueous $HNO_3$, a number of complexes containing water are present:

(i) A very weak "complex" between toluene and water which accounts for the solubility of 0·017 M $H_2O$ in toluene,
(ii) a complex with a proportion (~20 per cent) of the "free" HDBP, i.e. HDBP not complexed with $HNO_3$ assuming a 1:1 ratio,
(iii) a complex with a proportion of the HDBP·$HNO_3$ complex, and
(iv) a complex, $(HNO_3)_2 \cdot H_2O$, with the $HNO_3$ extracted by the toluene.[10]

The approximate amounts of the above four types of water complex for the 0·5 M HDBP–toluene and 0, 6, 10 and 12 M $HNO_3$ are given in Table 4, in which it is assumed that the solubility of $H_2O$ in toluene is approximately the same in contact with $H_2O$ and with 12 M $HNO_3$. The mole ratio of $H_2O$ to $HNO_3$ for the HDBP·$HNO_3$ complex (iii) is 0·4 $\pm$ 0·06, i.e. 40 per cent of the complex is monohydrated.

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# COMPLEX FORMATION BETWEEN GLUCONIC ACID AND GERMANIC ACID

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**Abstract**—The germanium dioxide/gluconic acid system has been investigated in aqueous solution from pH 2 to 12. Solubility, pH, conductivity and optical rotation measurements have shown that germanic acid reacts with gluconic acid to form a 2:3 complex in the pH range 1·7–4. Between pH 4 and 6 a complex anion with a mole ratio of 1:1 can be identified. Above pH 11 it seems likely that a further complex anion is formed.

GLUCONATE complexes of many metals have been reported. Gluconic acid has an excellent chelating ability with many metals in basic media. More recently, studies have been extended to cover wide ranges of pH—for example, the lead and copper gluconate systems have been investigated by PECSOK and JUVET[1,2]. The antimony,[3] cadmium,[4] iron,[5] boron[6,7] and molybdenum[8] complexes of gluconic acid have also received attention. The germanium/gluconic acid system has not previously been reported in detail.

## EXPERIMENTAL

### *Materials*

Spectrographically pure quartz type $GeO_2$ (99·98 per cent) was used for all experiments.

Gluconic acid solutions were prepared by dissolving 1.5 gluconolactone (gluconic acid $\delta$ lactone) in conductivity water. Purity determined by titration was 100 per cent.

For some experiments calcium gluconate was used. Purity of this salt (determined by analysis for calcium) was 99·2 per cent.

The conductivity water used was prepared by passing distilled water through a mixed bed deionisation column. All solutions had a conductivity of 1·0–1·5 $\times$ $10^{-6}$ mhos at 21°C.

### *Methods*

*Solubility experiments.* The 0·06 g samples of quartz type $GeO_2$ were mixed with 3 ml of aqueous solutions of gluconic acid of various concentrations contained in 10 ml centrifuge tubes. These tubes were attached to the edge of a disk held vertically which was rotated slowly for one week at 20°C. Preliminary experiments indicated that the amount of germanium taken into solution increased with time, equilibrium being attained after 24 hr. After centrifuging, the amount of germanium taken into solution was estimated on an aliquot of the supernatant liquid, using the phenylfluorone method.[9] It had previously been ascertained that gluconic acid did not affect the phenylfluorone reagent.

*Conductivity and pH studies.* A method of continuous variations was used. 0·04 M gluconic acid was mixed in various molar proportions with an 0·04 M solution of $GeO_2$. A series of controls,

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[1] R. L. PECSOK and R. S. JUVET, *J. Amer. Chem. Soc.* **77**, 202–6 (1955).
[2] R. L. PECSOK and R. S. JUVET, *J. Amer. Chem. Soc.* **78**, 3967–72 (1956).
[3] G. PATRA and S. PANI, *J. Indian Chem. Soc.* **32**, 572–6 (1955).
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[5] R. L. PECSOK and J. SANDERA, *J. Amer. Chem. Soc.* **77**, 1489 (1955).
[6] J. G. CARRERO, *An. Soc. esp. Fis. Quim.* **48** B, 149–54 (1952).
[7] J. G. CARRERO, *An. Univ. Murcia* **15**, 41–117 (1955).
[8] E. RICHARDSON, *J. Inorg. Nucl. Chem.* **9**, 273–8 (1959).
[9] H. J. CLULEY, *Analyst* **76**, 523–30 (1951).

i.e. solutions containing gluconic acid alone, were prepared at the same time. The conductivities of the solutions were determined after four hours. In another experiment, the mixtures of 0·04 M $GeO_2$ and 0·04 M gluconic acid were heated on a boiling water bath for 2½ hr, cooled, made up to the required volume, allowed to stand for three days and then their pH values and conductivities determined.

A conductivity cell and standard Wheatstone bridge circuit as described by FINDLAY[10] was used, the balance point being detected by a cathode ray oscilloscope.[11] All measurements were made at 20 ± 0·1°C, and are given in $\Omega^{-1}$ cm$^{-1}$.

pH measurements were made on a Cambridge portable pH meter (range 0–14 pH) using a glass and calomel electrode system which was standardized with a British Drug Houses buffer of pH 4·0 or 6·5 at 21 or 25°C.

*Optical rotation experiments.* The optical activities of the mixtures of 0·04 M gluconic acid and 0·04 M $GeO_2$ made up for the conductivity and pH experiments were determined using a Hilger and Watts Standard Polarimeter Mark III. The average of ten to twelve rotation readings of each solution was used for the plot. Readings are given as rotation (in degrees) produced by the solution in a 4 dm tube using sodium light ($\lambda$ = 5893°A).

A similar series of readings was made on mixtures of 0·04 M calcium gluconate and 0·04 M $GeO_2$. In this case it was found necessary to filter all solutions before their optical rotations could be determined.

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*Potentiometric titrations.* A static constant volume method was used. An 0·08 M solution of the germanogluconic acid was prepared and 50 ml aliquots transferred to 100 ml graduated flasks. Varying amounts of approximately 0·32 M NaOH were added to each to give a range of values of mole ratios NaOH/Ge from 0 to 4·0. The contents of each flask were made up to 100 ml and the series then corresponded to the titration of 0·04 M germanogluconic acid by 0·04 M alkali at constant volume. The pH values of all the solutions were determined after 24 hr. The titration curve thus obtained corresponds to equilibrium conditions. A "blank" titration curve was also carried out by titrating gluconic acid by NaOH under the same conditions.

In order to follow the change in optical activity during titration, the optical rotation of these solutions was measured using the Hilger and Watts Standard Polarimeter.

## DISCUSSION AND RESULTS

The solubility of quartz type $GeO_2$ in solutions of gluconic acid is shown in Fig. 1. The amount of soluble germanium is plotted against the molar concentration of hydroxy acid. Over the sloping part of the curve excess solid $GeO_2$ is present, whilst over the horizontal part there is an excess of soluble acid in the presence of soluble germanium. Equilibrium occurs at a mole ratio Ge:gluconic acid of 2:3.

The results of pH, conductivity and optical rotation experiments on mixtures of 0·04 M gluconic acid and 0·04 M $GeO_2$ are given in Figs. 2, 3 and 4. The position of the maximum on the conductivity curve is quite well defined and occurs at a mole ratio Ge:gluconic acid of 2:3. This is supported by optical rotation studies (Fig. 4). The formation of a 2:3 complex around pH 2·0 is therefore indicated. The results of pH studies (Fig. 2) are not considered sufficiently sensitive to distinguish between the formation of a 2:3 complex and a 1:2 complex. In the experiment in which the mixtures of 0·04 M $GeO_2$ and 0·04 M gluconic acid were kept at boiling water bath temperature for 2½ hr, the conductivity curve showed a definite maximum at a mole ratio of 2:3 but the optical activity and pH plots did not distinguish between a 2:3 and a 1:2 complex.

The problem was investigated further using higher concentrations of $GeO_2$ and gluconic acid. Various quantities of solid $GeO_2$ were mixed with 0·1 M gluconic acid and water to give various molecular ratios of Ge:gluconic acid. The mixtures

[10] A. FINDLAY, *Pract. Phys. Chem.* 161 (1945).
[11] R. N. HASZELDINE and A. A. WOOLF, *Chem. & Ind.* (*Rev.*) 544–5 July 8th (1950).

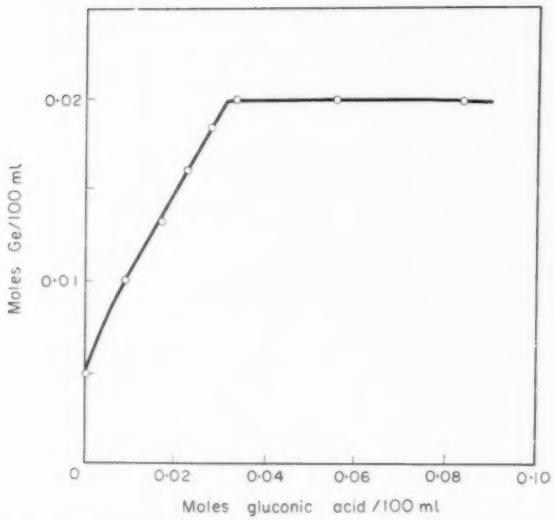


FIG. 1.—Solubility of quartz type $GeO_2$ in solutions of gluconic acid at 20°C.

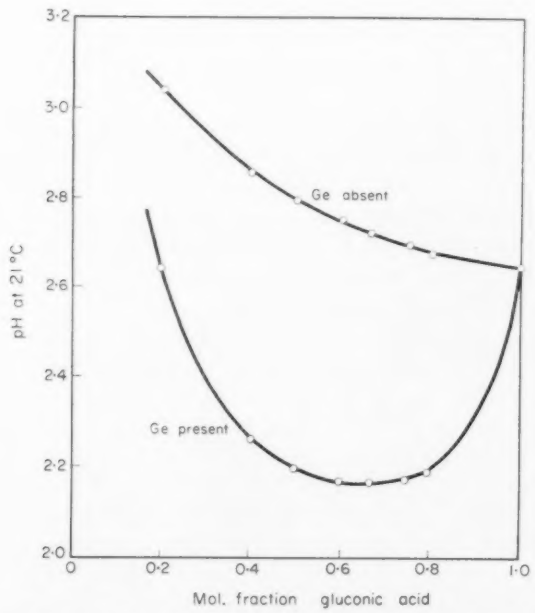


FIG. 2.—pH values of mixtures of 0·04 M gluconic acid and 0·04 M $GeO_2$ at 21°C.

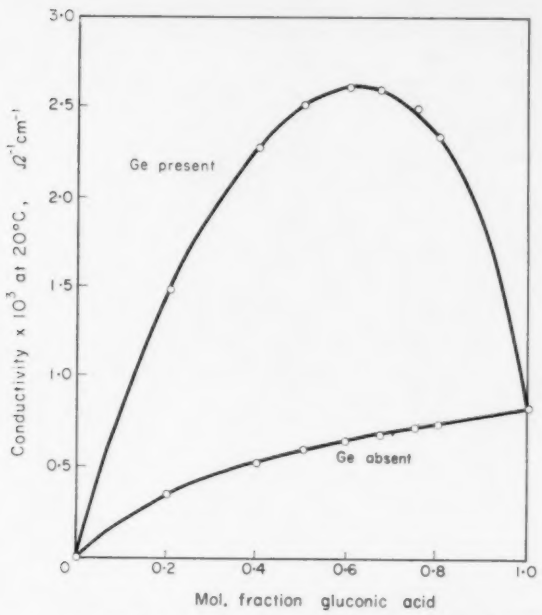


FIG. 3.—Conductivities of mixtures of 0·04 M gluconic acid and 0·04 M $GeO_2$ at 20°C.

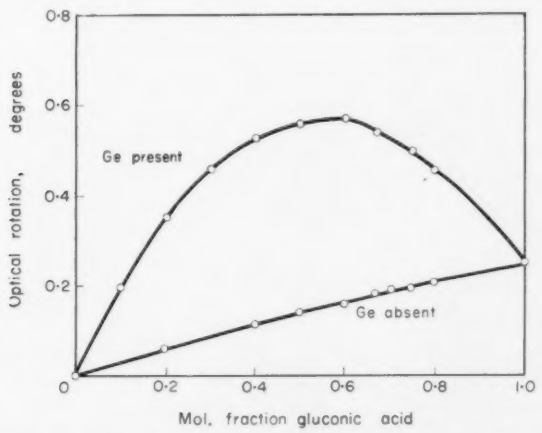


FIG. 4.—Optical activities of mixtures of 0·04 M gluconic acid and 0·04 M $GeO_2$ at room temperature. Rotation is given in degrees using a 4 dm tube and sodium light.

were shaken at room temperature for five days. At the end of this period the solutions were filtered and their pH values and optical activities determined. Results are given in Table 1 where it can be seen that the formation of a 2:3 complex is indicated.

The results of potentiometric titration of the complex acid and gluconic acid are given in Fig. 5. Clearly the titration curves for parent acid and complex acid are very different. They can be interpreted by the procedure recommended by GAGE.[12]

[12] J. C. GAGE, *Analyst* **82**, 219 (1957).



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TABLE 1

| Tube no. | Quartz-type $GeO_2$ (g) | 0·1 M gluconic acid (ml) | $H_2O$ (ml) | Mole ratio Ge/Acid | Rotation* | pH 21°C. |
|---|---|---|---|---|---|---|
| 1 | 0·2092 | 20 | 20 | 1:1 | 1·66† | 1·74 |
| 2 | 0·2092 | 30 | 20 | 2:3 | 1·70 | 1·71 |
| 3 | 0·1569 | 30 | 15 | 1:2 | 1·62 | 1·72 |
| 4 | 0·1046 | 30 | 10 | 1:3 | 1·52 | 1·74 |
| 5 | — | 0·1 N gluconic acid | — | — | 0·76 | 2·39 |

* 4 dm tube using sodium light, average of a dozen readings quoted.
† The liquid in Tube No. 1 was the only one containing solid matter, i.e. an excess of $GeO_2$.

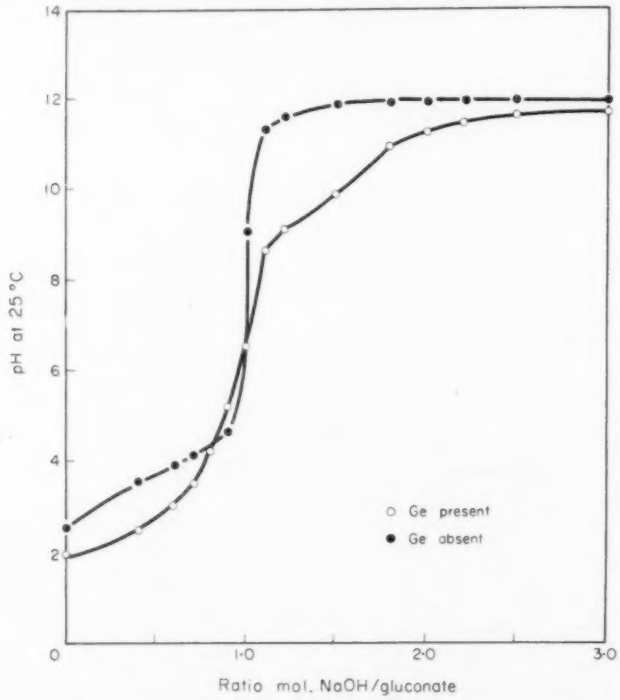



FIG. 5.—Potentiometric titration curves for gluconic acid and germanogluconic acid at 25°C.

A far more useful form of the Henderson equation can be obtained by rearranging it thus:

$$hx = Kc - Kx$$

where $K$ = the classical dissociation constant
$c$ = total concentration of acid
and $x = a + h - Kw/h$
where $a$ = concentration of added alkali
$h$ = hydrogen ion concentration
$Kw/h$ = hydroxyl ion concentration.

Thus a plot of $hx$ against $x$ should be a straight line of slope $K$. This is found to be so both for gluconic acid and the complex acid (Fig. 6). The plot of $hx$ against $x$ for the complex acid gives a straight line which intercepts the $x$ axis at a value of 0·029, corresponding to a NaOH/gluconate ratio of 0·72 or a NaOH/Ge ratio of 0·5. The indications are, therefore, that a salt containing one sodium atom for every two

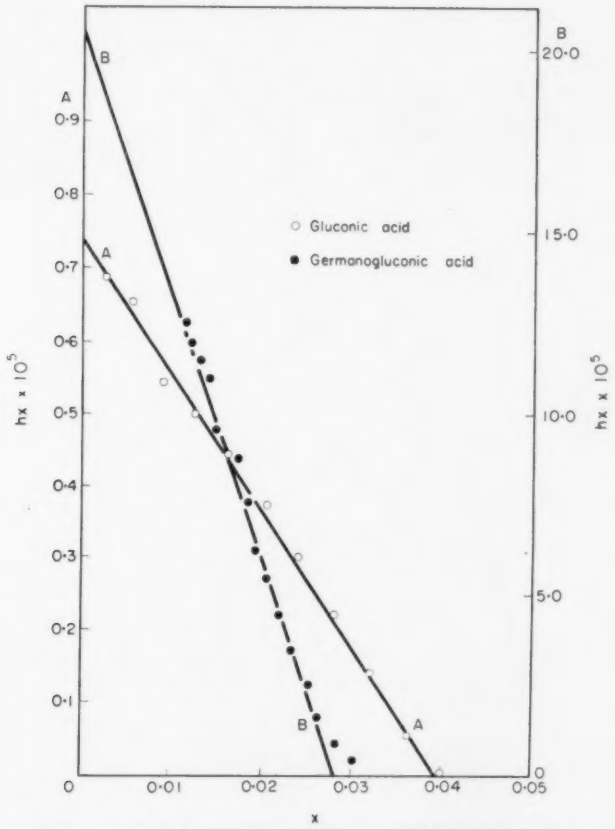


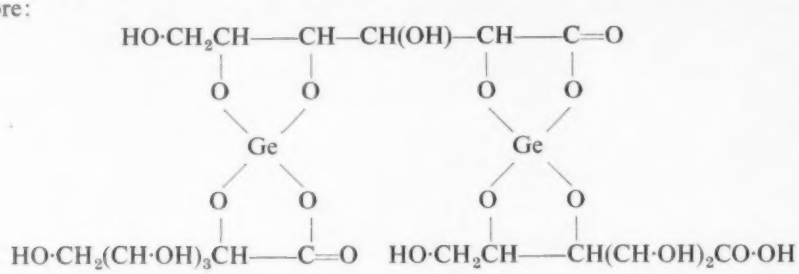

FIG. 6.—Plot of $hx$ against $x$ for gluconic acid (line A) and for germanogluconic acid (line B) at 25°C.

germanium atoms has been formed during titration. Thus the complex acid is monobasic.

The dissociation constant for the complex acid is $7{\cdot}7 \times 10^{-3}$ at 25°C. ($pK_a = 2{\cdot}11$ and ligand concentration 0·04 M). The dissociation constant of gluconic acid under the same conditions is $1{\cdot}84 \times 10^{-4}$ ($pK_a = 3{\cdot}74$).

Conductivity and optical rotation measurements have indicated that the complex acid consists of 2 mole Ge/3 mole gluconic acid; therefore complexing possibly takes place through hydroxyl groups (most probably *cis* OH groups) of one molecule of gluconic acid and through carboxylic and α-hydroxy groups of the other two

molecules of gluconic acid. The structural formula of the complex acid could be, therefore:



The optical activities of the mixtures of 0·04 M calcium gluconate and 0·04 M $GeO_2$ are shown in Fig. 7. Since calcium gluconate gives two molecules of gluconic

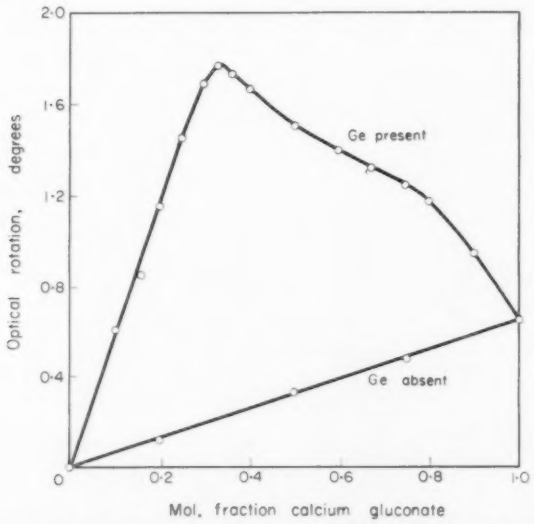



FIG. 7.—Optical activities of mixtures of 0·04 M calcium gluconate and 0·04 M $GeO_2$ solutions. Rotation is given in degrees using a 4 dm tube and sodium light.

acid on "hydrolysis", the maximum on this graph corresponds to 1 mole Ge/1 mole gluconic acid. The pH values of these solutions all lie in the 5·6–6·1 region. It therefore appears that before pH 5·0 is reached the Ge/gluconic acid complex of mole ratio 2:3 is replaced by a 1:1 complex. The actual pH value at which the transition starts to take place can be detected by potentiometric titration using a dynamic method. Using ligand concentrations of 0·04 M and 0·02 M it was shown that the solutions became unstable at pH 4·0. Equilibrium however was attained after 5 min. At about pH 8·0 the solutions once again reached equilibrium rapidly on the addition of the NaOH.

The change in optical rotation of germanogluconic acid and gluconic acid during titration with NaOH is given in Figs. 8 and 9. Optical rotation reaches a maximum value at a pH value in the neighbourhood of seven and a NaOH/gluconate ratio 1:1. The inflexion point at a molar ratio of NaOH/gluconate (see Fig. 8) of about 0·80

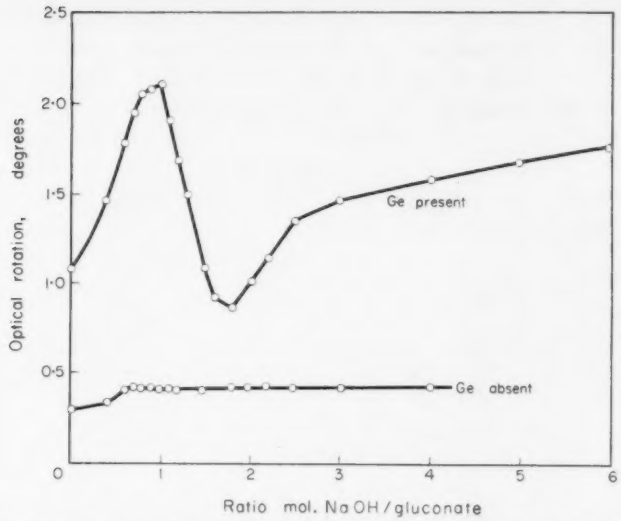



FIG. 8.—Change in optical rotation of 0·04 M germanogluconic acid and 0·04 M gluconic acid during titration with 0·04 M NaOH. Plot of optical rotation against ratio mole. NaOH added/ gluconate. Rotation is given in degrees using a 4 dm tube and sodium light.

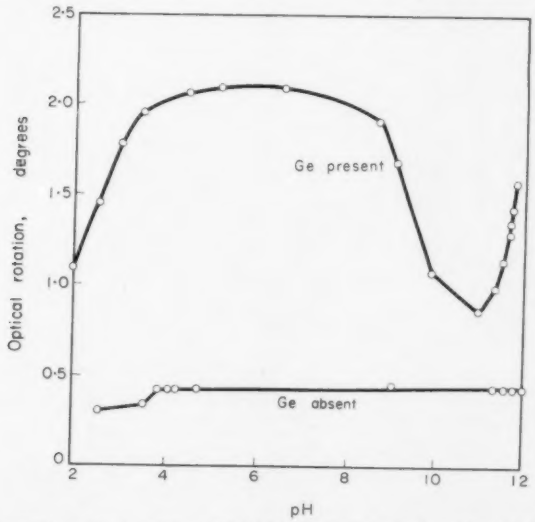



FIG. 9.—Change in optical rotation of 0·04 M germanogluconic acid and 0·04 M gluconic acid during titration with 0·04 M NaOH. Plot of optical rotation against pH. Rotation is given in degrees using a 4 dm tube and sodium light.

(pH 4·0) is significant and is possibly the point at which the formation of the 1:1 complex starts to occur. This is in agreement with the observations made during the dynamic titration experiment.

Since the optical rotation reaches a maximum value in the neighbourhood of pH 7 the formation of the 1:1 complex is possibly complete in this pH region. The experiments with calcium gluconate and $GeO_2$ also indicate that the 1:1 complex is the major species at pH 6. The decrease in optical rotation at pH values greater

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than eight could be partly due to the decomposition of the 1:1 complex anion, a process which is complete at about pH 10·9, i.e. the minimum point on the curve. However, at this pH value the optical activity of the $GeO_2$/gluconic acid solutions is higher than that for gluconic acid alone. Hence a complex anion must exist in solution. From the information available it is not possible to determine when the 1:1 complex starts to be replaced by another complex anion but since the optical activity increases again above pH 10·9 (Fig. 9) it appears likely that a new complex anion must be present above this value.

J. Inorg. Nucl. Chem., 1961, Vol. 21, pp. 375 to 384. Pergamon Press Ltd. Printed in Northern Ireland

# NOTES

## Co-precipitation of francium and caesium with heteropolyacids

(*Received* 1 *March* 1961; *in revised form* 15 *June* 1961)

HETEROPOLYACIDS have long been used for separation of heavy alkali elements by precipitation e.g. the isolation of $^{137}Cs$ from uranium fission products.[1–5] The small solubility of some heteropolyacids (abbreviated as HPA) in strong mineral acids enables specific coprecipitation even of trace quantities of caesium[6] and of francium.[7–9]

Besides HPA derived from two acid residues, which are used in most cases, more complex tri-HPA may be also used.[6,10] The separation of rubidium and caesium[10] and the caesium-francium pair might be expected.

The aim of this work was the systematic testing of precipitation of very small quantities of francium and caesium with di-HPA under various reaction conditions and the determination of the degree of coprecipitation with some tri- and tetra-HPA with various central atoms and ligands.

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## EXPERIMENTAL

### *Materials*

*Francium and caesium.* The radioactive isotopes of both these elements were isolated from a thorium target, which was irradiated for 15–20 min with protons of 660 MeV energy from the synchrocyclotron of the Joint Institute of Nuclear Research at Dubna, USSR, by the method described elsewhere.[8] The final solution contained approximately $10^{-14}$ g of francium, which was composed of isotopes $^{222}Fr > ^{223}Fr > ^{212}Fr$,[11] and about a ten times higher quantity of caesium isotopes. The 20 min $^{212}Fr$ is the only $\alpha$-emitter among these isotopes, and the $\beta$-activity is mostly due to the $^{136}Cs$ and $^{137}Cs$. It is possible therefore to determine both the francium and caesium content from one sample.

In the orientation experiments as well as in some other cases also $^{134}Cs$ and $^{137}Cs$ were used as tracers.

*Heteropolyacids.* The following HPA were used:

| | | | |
|---|---|---|---|
| 1. $H_3PW_{12}O_{40}.nH_2O$ | (HPW) | 11. $H_3AsMo_8W_4O_{40}.nH_2O$ | (HAsMoW I) |
| 2. $H_4SiW_{12}O_{40}$ | (HSiW) | 12. $H_3AsMo_6W_6O_{40}$ | (HAsMoW II) |
| 3. $H_3PMo_{12}O_{40}$ | (HPMo) | 13. $H_3AsMo_4W_8O_{40}$ | (HAsMoW III) |
| 4. $H_4SiMo_{12}O_{40}$ | (HSiMo) | 14. $H_3AsMo_{10}V_2O_{39}$ | (HAsMoV) |
| 5. $H_3PMo_{10}W_2O_{40}$ | (HPMoW I) | 15. $H_3AsW_{10}V_2O_{39}$ | (HAsWV) |
| 6. $H_3PMo_2W_{10}O_{40}$ | (HPMoW II) | 16. $H_5BW_{10}V_2O_{39}$ | (HBWV) |
| 7. $H_3PW_{10}V_2O_{39}$ | (HPWV) | 17. $H_4GeW_{10}V_2O_{39}$ | (HGeWV) |
| 8. $H_3PMo_{10}V_2O_{39}$ | (HPMoV) | 18. $H_4SeW_{10}V_2O_{39}$ | (HSeWV) |
| 9. $H_4SiW_{10}V_2O_{39}$ | (HSiWV) | 19. $H_3PMo_8W_2V_2O_{39}$ | (HPMoWV I) |
| 10. $H_4SiMo_{10}V_2O_{39}$ | (HSiMoV) | 20. $H_3PMo_6W_4V_2O_{39}$ | (HPMoWV II) |


[1] M. H. FELDMAN and L. E. GLENDENIN, *NNES Part IV*, **9**, 654 (1951).
[2] P. E. CARTER, *AERE* C/R 1231 (1953).
[3] V. I. SPITSYN and N. B. MIKHEEV, *Atomnaya Energia* **3**, 255 (1957).
[4] A. RAGGENBASS, M. QUISNCY, J. FRADIN and J. DUFRENE, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva* 1958. Paper 1179 United Nations (1959).
[5] T. V. HEALY, B. L. DAVIES and G. INGHAM, AERE/C/R 2528, 2577, 2594 (1958); AERE/C/R 2621 (1959); AERE/R 2968 (1959).
[6] V. KOUŘIM, *J. Inorg. Nucl. Chem.* **12**, 370 (1960).
[7] E. K. HYDE, *J. Amer. Chem. Soc.* **74**, 4181 (1952).
[8] A. K. LAVRUKHINA and S. S. RODIN, *Trudy komisii Anal. Khim.* **12**, 274 (1958).
[9] A. K. LAVRUKHINA, *Uspecki Khim.* **27**, 10, 1209 (1958).
[10] V. KOUŘIM and A. K. LAVRUKHINA, *Zh. Anal. Khim.* **15**, 3, 272 (1960).
[11] A. K. LAVRUKHINA and S. S. RODIN, *Radiokhimia* **2**, 83 (1960).

The compounds 1–4 were obtained by purifying commercial products, others were synthesized.* They were analysed by standard methods or colorimetrically.[6]

*Acids.* Mineral acid solutions were made up from fuming nitric acid and hydrochloric acid saturated with HCl gas (13 N).

*Methods*

*Francium and caesium coprecipitation with heteropolyacids.* Fifty milligrams of HPA were dissolved in a micro test tube by adding 0·03 ml of Fr and Cs solution. The solution was precipitated with 0·33 ml of 12 N HCl or $HNO_3$, the precipitate was mixed for 5 min and centrifuged. Some experiments were performed in such a manner that different fractions of the HPA present were precipitated either by varying the concentration of the mineral acid or by varying the starting amount of HPA. The 0·02 ml samples were taken from the centrifugate and examined for $\alpha$- and some hours later for $\beta$-activity by standard methods.

*Coprecipitation with carrier.* The process was substantially the same as in the former case. Only 10 N HCl was used so that the differences could be more evident, and the carrier was added as K, Rb or Cs chloride with the acid. The amount of carrier was chosen so that the ratio of one mole HPA to one gramme-atom K, Rb or Cs was attained. Some experiments were performed using 2 and 0·1 gramme-atoms of alkali.

## RESULTS AND DISCUSSION

*Coprecipitation*

Table 1 shows the coprecipitation yields from 12 N HCl and $HNO_3$. The highest yields were obtained with di-HPA (1, 2, 3, 4), with tri-HPA, where W and Mo ligands were bonded to a central P or As atom (5, 6, 11, 12, 13), and with AsWV. The lowest yields occurred with HPA with central B,

TABLE 1.—COPRECIPITATION OF CARRIER-FREE Fr AND Cs WITH HETEROPOLYACIDS†

| | | Fr | | | | Cs | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | HCl | | $HNO_3$ | | HCl | | $HNO_3$ | |
| | % | HPA | Act. | HPA | Act. | HPA | Act. | HPA | Act. |
| 1. Di-HPA | HPW | 99·5 | 98·7 | 96· | 95·8 | 99·5 | 97·7 | 96· | 97·2 |
| 2. | HSiW | 78· | 98·3 | 0· | 0· | 78· | 96·9 | 0· | 0· |
| 3. | HPMo | 90· | 98·4 | 30· | 93·0 | 90· | 95·1 | 30· | 92·9 |
| 4. | HSiMo | 96· | 96·9 | 36· | 80· | 96· | 93·6 | 36· | 75· |
| 5. Tri-HPA | HPMoW I | 92· | 97·3 | 20· | 86· | 92· | 96·1 | 20· | 86· |
| 6. | HPMoW II | 96· | 95·6 | 78· | 93·5 | 96· | 96·9 | 78· | 94·7 |
| 7. | HPWV | 15· | 82· | 0· | 0· | 15· | 79· | 0· | 0· |
| 8. | HPMoV | 65· | 87· | 70· | 46· | 65· | 83· | 70· | 42. |
| 9. | HSiWV | 0· | 0· | 0· | 0· | 0· | 0· | 0· | 0· |
| 10. | HSiMoV | 82· | 85· | 82· | 32· | 82· | 81· | 82· | 38· |
| 11. | HAsMoW I | — | 91·5 | 0· | 0· | — | 89· | 0· | 0· |
| 12. | HAsMoW II | — | 94·5 | 0· | 0· | — | 94·5 | 0· | 0· |
| 13. | HAsMoW III | — | 91·5 | 57· | 75· | — | 87· | 57· | 40· |
| 14. | HAsMoV | — | 82· | 82· | 57· | — | 71· | 82· | 51· |
| 15. | HAsWV | — | 97· | 0· | 0· | — | 98·5 | 0· | 0· |
| 16. | HBWV | — | 77· | 15· | 39· | — | 64· | 15· | 30· |
| 17. | HGeWV | — | 68· | 0· | 0· | — | 32· | 0· | 0· |
| 18. | HSeWV | — | 84· | 93· | 56· | — | 79· | 93· | 49· |
| 19. Tetra-HPA | HPMoWV I | 78· | 92· | 50· | 74· | 78· | 87· | 50· | 59· |
| 20. | HPMoWV II | 65· | 81· | 0· | 0· | 65· | 66· | 0· | 0· |

* Some HPA were obtained by courtesy of Prof. KOKORIN from Kishinev State University.

† % HPA–fraction of the precipitated heteropolyacids
% Act–fraction of the captured activity of Fr and Cs isotopes

Ge or Se atoms. No precipitate appeared with HSiWV even in the concentrated acids. In most cases the presence of vanadium in the HPA molecule leads to lower yields.

Hydrochloric acid may be used as a rule more advantageously than nitric acid of the same concentration, where the HPA are more soluble.[6] The anion of the mineral acid present may be important for the precipitate formation. Though about equal HPA amounts were precipitated with HPMoV and HSiMoV in HCl and $HNO_3$ media, the amount of Cs and Fr captured in $HNO_3$ was about half that in HCl.

Francium is better precipitated than caesium, but there is no substantial difference except when using HPA 13, 17, 18 and 20. This may be due to the small difference between the Fr and Cs ionic radii. In further experiments we did not succeed in the mutual separation of Cs and Fr either by repeated precipitation or by column chromatography with ammonium salts of the heteropolyacids, for the same reason.

Tables 2 and 3 show the dependence of the degree of coprecipitation of Fr and Cs on the amount of precipitated HPA. The decrease of the HPA solubility in higher $HNO_3$ concentrations together with the increase of Cs and Fr captured may be seen from the results with HSiW and HSiMo. This effect is not so clear with HPW of a very low solubility in $HNO_3$ and with the unstable HPMo.

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TABLE 2.—COPRECIPITATION OF CARRIER FREE Fr AND Cs WITH HETEROPOLYACIDS IN $HNO_3$ OF VARIOUS CONCENTRATIONS. (CONSTANT HETEROPOLYACID AMOUNT)*

| | HPA (mg) | $HNO_3$ (N) | HPA (%) | Fr (%) | Cs (%) |
|---|---|---|---|---|---|
| HSiW | 50 | 11·8 | 0 | 0 | 0 |
| | 50 | 12·7 | 0 | 0 | 0 |
| | 50 | 14·5 | 0 | 0 | 0 |
| | 50 | 20·2 | 71 | 87 | 88 |
| HPW | 50 | 11·8 | 95 | 96·1 | 93·1 |
| | 50 | 12·7 | 96 | 95·8 | 97·2 |
| | 50 | 14·5 | 93 | 91·0 | 91·5 |
| | 50 | 20·2 | 96 | 93·0 | 93·4 |
| HSiMo | 50 | 11·8 | 10 | 81 | 70 |
| | 50 | 12·7 | 36 | 80 | 75 |
| | 50 | 14·5 | 57 | 83 | 77 |
| | 50 | 20·2 | 82 | 86 | 89 |
| HPMo | 50 | 11·8 | 4 | 91·4 | 87 |
| | 50 | 12·7 | 30 | 93·0 | 92·9 |
| | 50 | 14·5 | 44 | 92·1 | 89 |
| | 50 | 20·2 | 78 | 93·9 | 90·8 |

* % HPA–fraction of the heteropolyacid precipitated
% Fr, Cs–fraction of Fr and Cs coprecipitated.

At a certain mineral acid concentration a corresponding minimum amount of HPA is necessary to form the precipitate. This threshold amount is usually larger than would correspond to the solubility only and it is characteristic of the way in which it was produced. It was determined that although the reaction proceeds quite quickly at the beginning, the maximum HPA amount was not precipitated until 20 min after mixing with the mineral acid, and maximum yields of coprecipitated alkali elements were attained in the next 10–20 min after that. During our work it was not possible to wait too long owing to the short half-life of $^{212}$Fr, and the measured values correspond therefore to non-equilibrium conditions. By carefully watching the operation conditions, reproducible values were attained.

It was not possible to characterize the degree of coprecipitation by Chlopin or Doerner-Hoskins coprecipitation constants[12] but comparing the fraction of the HPA precipitated with the fraction of

[12] I. E. STARIK: *Osnovy radiokhimii*, p. 210, Izd. Acad. Nauk USSR, Moscow-Leningrad (1959).

TABLE 3.—COPRECIPITATION OF CARRIER-FREE Fr AND Cs WITH VARIOUS AMOUNTS OF HETEROPOLYACIDS. (CONSTANT HCl CONCENTRATION)*

| | HPA (mg) | HCl (N) | HPA (%) | Fr (%) | Cs (%) |
|---|---|---|---|---|---|
| HSiW | 5·0 | 12·3 | 0 | 0 | 0 |
| | 11·2 | 12·3 | 20 | 98·3 | 94·0 |
| | 20·8 | 12·3 | 65 | 98·6 | 95·0 |
| | 49·9 | 12·3 | 86 | 98·7 | 98·4 |
| HPW | 5·3 | 12·3 | 94 | 96·2 | 94·2 |
| | 9·9 | 12·3 | 97 | 96·5 | 96·6 |
| | 19·7 | 12·3 | 98 | 97·9 | 97·8 |
| | 49·8 | 12·3 | 99 | 98·2 | 97·6 |
| HSiMo | 35·0 | 12·3 | 80 | 91·8 | 87 |
| | 50·0 | 12·3 | 96 | 96·9 | 93·6 |
| | 50·0† | 12·3 | 77 | 86 | 77 |
| HPMo | 32·0 | 12·3 | 77 | 92·0 | 90·1 |
| | 50·0 | 12·3 | 90 | 98·4 | 95·1 |
| | 50·0† | 12·3 | 78 | 91·7 | 92·1 |

* % HPA–fraction of the heteropolyacid precipitated
% Fr, Cs–fraction of Fr and Cs coprecipitated.
† Precipitated for 3 min only; other samples 5 min.

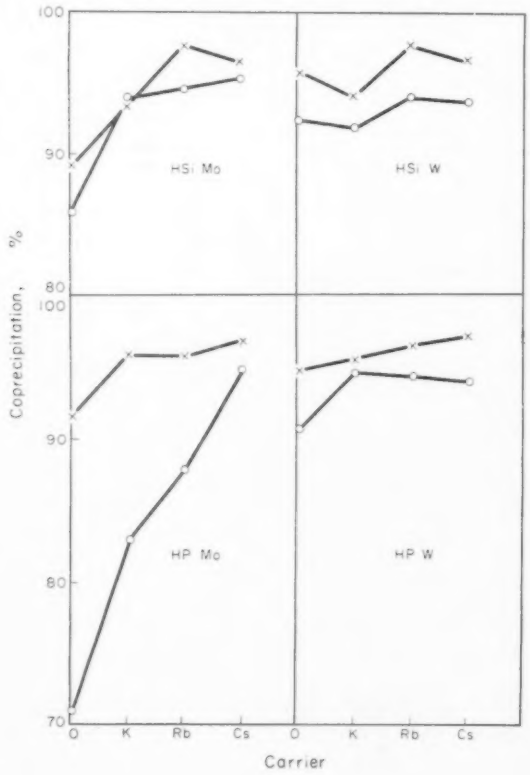


FIG. 1.—Coprecipitation of francium and caesium without and with carriers. Fr indicated by ×, Cs indicated by ○. HCl concentration 10 N, ratio mole HPA: g-atoms (K, Rb, Cs) = 1:1

the Cs and Fr activities captured by them, we can arrange the HPA into groups of those of a "high" and "low capacity" for alkalies in trace amount. All the di-HPA and the tri-HPA with tungsten as ligand fall into the first group; into the second fall the tri-HPA with Mo as ligand in $HNO_3$. An advantageous property of the HPA of the first group, especially of HPW, is their ability to capture the Cs and Fr present to a high degree at the time when the first HPA fraction is precipitated.

*Coprecipitation with carrier*

The problem of using a non-isotopic carrier to coprecipitate Fr with several HPA was studied earlier.[8,13] It was found that Cs as a carrier decreases in some cases the yields of coprecipitated Fr.

Our results are shown in Fig. 1. The carrier effect is relatively weakest with the least soluble HPW, and its influence is more important with the more soluble HSiMo and HPMo. In the case of HPMo, the carrier stabilizes this heteropolyacid, for the salt formed is resistant against the decomposing action of the concentrated HCl. Whereas the HPA with central P atoms show an increasing influence of carrier in the series K < Rb < Cs on the amounts of coprecipitated Fr and Cs, the HPA with central Si atoms show a surprising maximum coprecipitation of Fr on a Rb-carrier, and a decrease with K-carrier (HSiW). The reason may be in the spatial arrangement of the crystal lattices of HPA and their salts. Quantitative differences between our values and those of paper (13) are caused by different coprecipitation procedures.

As for the amount of carrier used, the experiments were carried out with molar ratios of 1 HPA: 2 Me, 1 HPA:1 Me and 1 HPA:0·1 Me. In most cases, higher yields resulted from the ratios 1:1 and 1:0·1 than from the ratio 1:2. The HPA have the tendency to form salts with lower alkali element content in a strong acid medium, and if the amount of alkali element present is higher, part remains in the solution and holds back the microamounts of the radioisotope.

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[13] A. K. Lavrukhina, A. A. Pozdnjakov and S. S. Rodin, *Intern. J. Appl. Radiation and Isotopes*, **9**, 34 (1960).

## A note on peroxy-oxalates of uranium

(*Received* 3 *July* 1961)

Rosenheim and Daehr[1] reported that a crystalline uranium peroxide of the composition $UO_4 \cdot 3H_2O$ could be obtained by the action of hydrogen peroxide on a solution of ammonium uranyl oxalate, while Hamaker and Koch[2] under similar conditions obtained a compound having the composition $(NH_4)_2U_2O_8C_2O_4(3\text{–}4)H_2O$. In the course of the present author's investigations[3] on the peroxy-compounds of uranium the formation of peroxy-oxalates was also studied, and it was found that pH played an important role in the formation of uranium peroxy-oxalates of different compositions. The reults are briefly reported here.

The work of Rosenheim and Daehr was repeated and the product obtained was $(NH_4)_2U_2O_8C_2O_4 \cdot 4H_2O$ (Found: U 59·33%, peroxide oxygen 4·0%, oxalate ($C_2O_4^{2-}$) 11%: calculated U 59·5%, peroxide oxygen 4·0%, oxalate ($C_2O_4^{2-}$) 11%), confirming the results of Hamaker and Koch. A solution of ammonium uranyl oxalate when treated with excess hydrogen peroxide showed a deeply-coloured solution in the pH range 4–8·5, the colour of the solution changing from yellow to orange with increase in pH. Below pH 4 and above pH 8·5 precipitation took place. The solids obtained by precipitation at pH 1 and 10 and by the addition of alcohol in the range pH 5–7 had the following composition:

[1] A. Rosenheim and H. Daehr, *Z. Anorg. Allgem. Chem.* **181**, 177–82 (1929).
[2] J. W. Hamaker and C. W. Koch, MDDC–1211 (1947).
[3] V. V. Dadape and N. S. Krishna Prasad, II Geneva Conference on Peaceful Uses of Atomic Energy P/1668, Vol. 4, 125–132 (1958).

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| Number | pH of precipitation | U per cent | Peroxide oxygen (O*) per cent | $C_2O_4^{2-}$ per cent | $U:O^*:C_2O_4^{2-}$ |
|---|---|---|---|---|---|
| 1 | 1 | 58·03 | 1·92 | 21·45 | 2:1:2 |
| 2 | 5–7 | 49·26 | 3·3 | 18·25 | 1:1:1 |
| 3 | 10 | 62·81 | 4·16 | — | 1:1:0 |

Preliminary studies on the absorption spectra of mixtures of uranyl nitrate, ammonium oxalate and hydrogen peroxide indicated the formation of a complex. Mixtures of uranyl nitrate and ammonium oxalate solutions alone showed two absorption peaks at 315 m$\mu$ and 415 m$\mu$ while the addition of hydrogen peroxide increased the optical density of the solution, the maximum absorption being at 340 m$\mu$. The absorption measurements also indicate that the formation of the complex is negligible below pH 4·0 and a maximum at about pH 8·0. Colorimetric titrations within this pH range indicated the formation of a complex of the composition $U:O^*:C_2O_4::1:1:2$ in solution. The work is in progress and details will be published later.

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## X-ray diffraction studies on compounds related to uranium trioxide dihydrate

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It has been observed[1,2] that the yellow precipitates initially formed by adding alkali to solutions of uranyl salts give similar diffraction patterns to that of the hydrate $UO_3.2H_2O$.[3] The present Note is concerned with the crystal structure of these compounds, and in particular with that of the so-called ammonium diuranate, the orange-yellow material formed when ammonia is the precipitating agent.

Under conditions of rapid precipitation, the products tend to be poorly crystalline, giving X-ray diffraction patterns consisting of relatively few, somewhat diffuse reflections. However, by adding a quantity of ammonia just insufficient to produce a permanent precipitate, and allowing the solution to stand, a highly crystalline product (of approximate composition $UO_3.1\frac{3}{4}H_2O.\frac{1}{4}NH_3$) has been obtained. It has proved possible to index the diffraction pattern of this compound and hence to determine the unit cell dimensions.

All the stronger lines on the pattern can be indexed on the basis of an orthorhombic face-centred cell with the following dimensions: $a = 7{\cdot}16 \pm 0{\cdot}01$ Å, $b = 4{\cdot}07 \pm 0{\cdot}01$ Å, $c = 7{\cdot}53 \pm 0{\cdot}01$ Å.

To account for the weaker lines on the pattern, a cell with a trebled $b$ axis and a doubled $c$ axis is necessary. The true cell, therefore, has the following dimensions: $a = 7{\cdot}16$ Å, $b = 12{\cdot}21$ Å, $c = 14{\cdot}06$ Å.

The agreement between $\sin^2\theta$ (observed) and $\sin^2\theta$ (calculated) is seen to be good from the Table.

The small pseudo-cell could accommodate two formula units of composition $UO_3$, $\sim 1\frac{3}{4}H_2O.\sim\frac{1}{4}NH_3$ and the large true cell 12 formula units. The cell plan perpendicular to the $c$ axis bears a marked resemblance to that of $U_3O_8$[$a = 6{\cdot}718$ Å, $b = 11{\cdot}97$ Å].[4] In each instance the basic cell is face-centred orthorhombic with $a/b$ close to $\sqrt{3}$, so that it can be thought of as a slight distortion of a simpler hexagonal cell. Secondly, in both instances there is a superlattice with a trebled $b$ spacing.

[1] C. A. Wamser, J. Belle, E. Bernsohn and B. Williamson. *J. Amer. Chem. Soc.*, **74**, 1070 (1952).
[2] P. S. Gentile, L. H. Talley and T. J. Collopy. *J. Inorg. Nucl. Chem.* **10**, 110 (1958).
[3] J. K. Dawson, E. Wait, R. Alcock and D. R. Chillon. *J. Chem. Soc.* 3531 (1956).
[4] R. R. Hoekstra, S. Siegel, L. H. Fuchs and J. J. Katz, *J. Phys. Chem.* **59**, 136 (1955).

TABLE —THE POWDER PATTERN OF $UO_3.\sim1\frac{1}{4}H_2O.\sim NH_3$

| Intensity | $d$ (Å) | $hkl$ | $\sin^2\theta$ (obs.) | $\sin^2\theta$ (calc.) |
|---|---|---|---|---|
| vvw | 9·48 | 011 | 66 | 66 |
| vs | 7·55 | 002 | 105 | 105 |
| vvw | 6·13 | 020 | 158 | 160 |
| vw | 5·72 | 111 | 181 | 182 |
| vw | 4·77 | 112 | 260 | 261 |
| vw | 4·63 | 013 | 276 | 276 |
| m | 3·766 | 004 | 419 | 419 |
| m | 3·579 | 200 | 464 | 464 |
| s | 3·535 | 130 | 476 | 475 |
| vvw | 3·407 | 123 | 512 | 512 |
| m | 3·233 | 202 | 569 | 569 |
| s | 3·200 | 132 | 580 | 580 |
| vvw | 3·054 | 040 | 638 | 638 |
| vvw | 3·024 | 220 | 650 | 650 |
| vvw | 2·928 | 015 | 693 | 695 |
| vvw | 2·854 | 222 | 730 | 729 |
| vvw | 2·829 | 042 | 742 | 743 |
| w | 2·593 | 204 | 883 | 883 |
| m | 2·576 | 134 | 895 | 894 |
| vw | 2·509 | 006 | 943 | 943 |
| vw | 2·322 | 026, 240 | 1103 | 1102 |
| vw | 2·310 | 150 | 1114 | 1113 |
| vvw | 2·215 | 242 | 1210 | 1207 |
| vvw | 2·212 | 152 | 1215 | 1218 |
| vw | 2·122 | 017 | 1320 | 1323 |
| m | 2·055 | 330 | 1403 | 1403 |
| mw | 2·049 | 136 | 1416 | 1418 |
| vw | 2·036 | 060 | 1434 | 1436 |
| w | 1·985 | 332 | 1508 | 1508 |
| vw | 1·967 | 062 | 1536 | 1541 |
| vvw | 1·954 | 127 | 1556 | 1559 |
| vvw | 1·885 | 008, 063 | 1674 | 1676, 1672 |
| w | 1·806 | 334 | 1823 | 1822 |
| w | 1·789 | 400, 064 | 1857 | 1856 |
| vw | 1·770 | 260 | 1898 | 1900 |
| vw | 1·742 | 402 | 1961 | 1960 |
| w | 1·722 | 262 | 2002 | 2004 |
| w | 1·704 | 246 | 2043 | 2045 |
| w | 1·693 | 170 | 2073 | 2070 |
| w | 1·664 | 352 | 2146 | 2146 |
| vw | 1·654 | 172 | 2172 | 2175 |
| vw | 1·617 | 404 | 2273 | 2275 |
| vvw | 1·603 | 048 | 2314 | 2314 |

The relationship between the three cells is illustrated in the Figure. The resemblance, however, goes further than merely the cell shape. The similarity of the relative intensities of the $hk0$ reflections in the two compounds suggests that the $u,v$ co-ordinates of the uranium atoms must be similar. Finally the high intensity of the 001 reflection indicates that the uranium atoms lie on the 001 planes. It seems likely, then, that the uranium atoms occupy the positions 000, $\frac{1}{2}\frac{1}{2}0$ in the smaller orthorhombic unit.

With changes in conditions of precipitation, variations in the composition of the ammonia precipitates are found, together with modifications of the diffraction pattern. Differences of about

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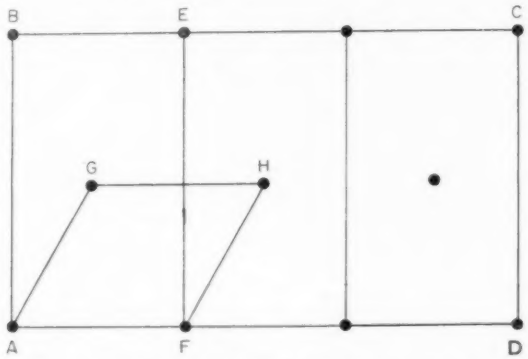
2 per cent in the *a* and *b* axes and of about 4 per cent in the *c* axis have been found between one sample and another. A systematic investigation of the dependence of cell dimensions on ammonia or water content has not been made, but it has been observed that, in general, there is a decrease in cell volume with increasing ammonia content. Since the $NH_3$ group has a larger volume than $H_2O$, it seems that variations in the composition of ammonium diuranates do not occur by simple one-for-one substitutions of water molecules by $NH_3$ groups.




FIGURE—Relationship between the true and pseudo cells of compounds of the type $UO_3.2H_2O$.
ABCD = true cell
ABEF = pseudo-cell
AGHF = pseudo-hexagonal cell

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## The infrared spectra of complexes containing pyridine

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DURING an investigation of the infra-red spectra of thiocyanate complexes[1] pyridine bands were observed in some of the complexes which contained ligand pyridine or the pyridinium cation. The results are of interest in the context of recent publications on the infra-red spectra of complexes containing pyridine.[2]

The positions of the pyridine bands in the infra-red spectra of the complexes are given in Table I in a sequence corresponding with the assignments of GILL *et al.*[2] The positions of the bands in the pyridine complexes of iron, nickel, copper and cadmium agree closely with the band positions given by these authors; the spectra of the remaining complexes have not previously been published.

The results show clearly the differences between the band positions in ligand pyridine (py) and the pyridinium cation (pyH):

(1) The bands in the region 1600–1400 $cm^{-1}$ (arising from in-plane ring deformations with C–C and C–N stretching) are shifted to lower frequencies in ligand pyridine compared with the pyridinium cation:

| | | | | |
|---|---|---|---|---|
| pyH | 1630s | 1600s | 1530s | 1480s |
| py ligand | 1600s | 1570w | 1490s | 1440s. |

There is a very weak band at 1630 $cm^{-1}$ in ligand pyridine.

[1] P. C. H. MITCHELL and R. J. P. WILLIAMS, *J. Chem. Soc.* 1192, (1960).
[2] N. N. GREENWOOD and K. WADE, *J. Chem. Soc.* 1130 (1960); N. S. GILL, R. H. NUTTALL, D. E. SCAIFE, D. W. A. SHARP, *J. Inorg. Nucl. Chem.* **18,** 79 (1961).

TABLE 1*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $Fepy_4(NCS)_2$ | 1631vw | 1600s | 1573w | | 1486s | 1442s | |
| $Nipy_4(NCS)_2$ | 1632vw | 1603s | | | 1488s | 1445s | |
| $Cupy_2(NCS)_2$ | 1632vw | 1601s | 1575w | | 1487s | 1447s | |
| $Znpy_2(NCS)_2$ | | 1612s | | | 1488s | 1447s | |
| $Cdpy_2(NCS)_2$ | 1633vw | 1600s | 1573w | | 1484s | 1444s | |
| $MoBr_3py_3$ | 1632vw | 1600s | | | 1486s | 1445s | |
| $(pyH)_3Cr(NCS)_6$ | 1629s | 1597s | | 1527s | 1480s | | 1418vw |
| $(pyH)_3Mo(NCS)_6$ | 1634s | 1600s | | 1527s | 1481s | | 1418vw |
| $(pyH)_2Mo(NCS)_6$ | 1631s | 1595s | | 1520s | 1481s | | 1418vw |
| $(pyH)_4Mo_2O_4(NCS)_6$ | 1630s | 1595s | | | 1479s | | |
| $Fepy_4(NCS)_2$ | 1356vw | | 1232vw | 1214s | | 1148m | 1068s |
| $Nipy_4(NCS)_2$ | 1356vw | | 1242vw | 1215s | | 1151m | 1068s |
| $Cupy_2(NCS)_2$ | 1353vw | | 1238vw | 1214s | | 1151m | 1071s |
| $Znpy_2(NCS)_2$ | 1360vw | | 1242vw | 1215s | | 1153m | 1068s |
| $Cdpy_2(NCS)_2$ | | | 1236vw | 1217s | | 1151m | 1071s |
| $MoBr_3py_3$ | | | | 1214s | | 1147m | 1068s |
| $(pyH)_3Cr(NCS)_6$ | 1365vw | 1328vw | 1236m | | 1195m | 1160m | |
| $(pyH)_3Mo(NCS)_6$ | 1368vw | 1325vw | 1235m | | 1195m | 1160m | |
| $(pyH)_2Mo(NCS)_6$ | 1365vw | 1321vw | 1235m | | 1189m | 1156m | |
| $(pyH)_4Mo_2O_4(NCS)_6$ | | 1321vw | 1238m | | 1190m | 1159m | |
| $Fepy_4(NCS)_2$ | 1037s | 1006m | 765s | 755s | 710s | 698s | |
| $Nipy_4(NCS)_2$ | 1043s | 1010m | 769s | 758s | 713s | 700s | |
| $Cupy_2(NCS)_2$ | 1043s | 1015m | 756s | | | 691s | |
| $Znpy_2(NCS)_2$ | 1045s | 1017m | | 755s | | 700s | 688s |
| $Cdpy_2(NCS)_2$ | 1037s | 1010m | 769m | 754s | | 694s | |
| $MoBr_3py_3$ | 1043s | 1015m | 760s | | | 689s | |
| $(pyH)_3Cr(NCS)_6$ | very weak | | | 735s | | 696w | |
| $(pyH)_3Mo(NCS)_6$ | for pyH | | | 735s | | 696w | |
| $(pyH)_2Mo(NCS)_6$ | betwee | | | 723s | | 699w | |
| $(pyH)_4Mo_2O_4(NCS)_6$ | 1050 an | | | 740s | 719s | | 670s |
| | 850 | | | | | | |

* All values in $cm^{-1}$. vw = very weak, w = weak, m = medium, s = strong.

Similar, but smaller shifts were observed by GREENWOOD and WADE[2] for $py,BCl_3$ compared with py,HCl and $py,HBCl_4$ (except in the case of the pyH band at 1530 $cm^{-1}$ which is shifted to 1540 $cm^{-1}$ in $py,BCl_3$).

(2) In the region 1170–1270 $cm^{-1}$ (from C–H in-plane deformations) the band positions and relative intensities are:

| | | | |
|---|---|---|---|
| pyH | 1240m | 1200m | 1160m |
| py ligand | 1240vw | 1215s | 1150m. |

The band at 1215 $cm^{-1}$ in ligand pyridine is stronger than that at 1200 $cm^{-1}$ in the cation. If the assignments are correct the shifts in this region appear to be less than those observed by GREENWOOD.

(3) In the region 1050–1000 $cm^{-1}$ (from totally symmetric in-plane breathing frequencies) the bands in ligand pyridine are at 1070s, 1040s and 1015m $cm^{-1}$. Only very weak bands are observed for the cation in this region at *ca.* 1040, 1030 and 1000 $cm^{-1}$. Thus the bands appear to be at lower frequencies for the cation in agreement with GREENWOOD's observations.

(4) The strong bands at *ca.* 720–740 $cm^{-1}$ (from out-of-plane ring deformations) in pyH appear to be shifted to 760 $cm^{-1}$ in ligand pyridine. The strong bands near 700 $cm^{-1}$ (from out-of-plane ring deformations) in ligand pyridine are absent from the cation.

The differences between the infra-red spectra of ligand pyridine and the pyridinium cation should provide a means of distinguishing between the two possibilities in complexes where there is ambiguity. A detailed discussion of the structural origin of the differences is not yet possible. It may be significant that the band shifts to higher frequencies (compared with free pyridine) generally decrease in the

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order $H^+ > B >$ transition metals (especially for the ring deformation frequencies). This is the order which would be expected if the shifts arise from back co-ordination from the acceptor atom to an anti-bonding orbital of the pyridine (cf. metal carbonyls). The fact that the shifts with zinc are generally greater than with the other metals is consistent with this interpretation since the third ionization potential of zinc is greater than that of any of the other metals included. This interpretation assumes, of course, that there is no significant coupling of acceptor-atom-nitrogen vibrations with the pyridine vibrations (cf. ref. 2).

## EXPERIMENTAL

Infra-red spectra were measured with a Perkin-Elmer Recording Spectrophotometer, Model 21, with rock salt optics. The compounds were held in Nujol suspension.

Preparations were standard in all cases.[1]

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